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JAMES F. NORRIS, PH.D., CONSULTING EDITOR

THE COLLOIDAL SALTS

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THE COLLOIDAL SALTS

BY

HARRY BOYER WEISER

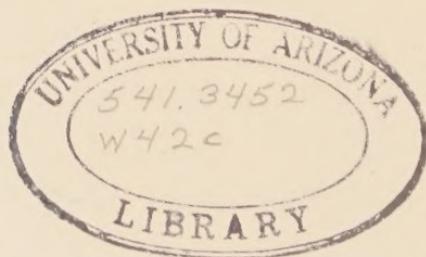
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PREFACE

Investigations on the colloidal character and applications of the inorganic salts are second in importance only to those on the hydrous oxides in the development of the modern theories of colloid chemistry. The present volume presents a critical summary of the colloidal behavior of the salts with particular reference to their role in the study of colloid chemical phenomena and to the theory underlying their technical applications.

The plan of the book is as follows: After a chapter dealing in a general way with the conditions of formation of colloidal salts, separate sections are given over to the colloidal sulfides, sulfates, halides, complex cyanides, silicates, and miscellaneous salts. The first portion of each section is devoted to a critical survey of the colloidal characteristics of the individual salts and the second portion to the general theory of the applications which are concerned with their colloidal behavior. In view of the comprehensive nature of the plan it is hoped that the volume will prove helpful to student and researcher in both theoretical and applied colloid science.

It is a pleasure to acknowledge gratefully the valued assistance of the following gentlemen who read and criticized certain portions of the manuscript: Wilder D. Bancroft of Cornell University, Robert H. Bogue of the United States Bureau of Standards, E. Newton Harvey of Princeton University, S. Edward Sheppard of the Eastman Kodak Company, and James E. Vail of the Philadelphia Quartz Company.

HARRY B. WEISER.

HOUSTON, TEXAS.
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THE COLLOIDAL SALTS

CHAPTER I

THE FORMATION OF COLLOIDAL SALTS

Two general methods of obtaining substances in the colloidal state may be distinguished: condensation or precipitation methods, and dispersion or peptization methods. In the condensation methods, substances in molecular solution interact under suitable conditions with the separation of a difficultly soluble body as a second phase. In the dispersion methods, conversely, the substance in mass is disintegrated or peptized by suitable means. The application of these general methods to the formation of colloidal salts will be considered in this chapter.

CONDENSATION METHODS

The Theory of von Weimarn.—The first systematic investigation of the form in which substances precipitate from solution was made by von Weimarn.¹ He calls attention to a number of different factors on which precipitation depends: the solubility of the substance, the latent heat of precipitation, the concentration at which the precipitation takes place, the normal pressure at the surface of the solvent, and the molecular weights of the solvent and the solute. He points out the impossibility of taking all of these factors into account and simplifies the problem by considering but two of the factors: the solubility of the precipitating substances, and the concentration at which precipitation begins. The process of condensation (precipitation) is considered as taking place in two stages: the first stage, in which the molecules condense to invisible or ultramicroscopic crystals; and the second, which is concerned with the growth of the

¹ *Kolloid-Z.*, **2**, 199, 230, 275, 301, 326; Supplement 2, LII; **3**, 89, 282 (1908); **4**, 27 (1909); "Grundzüge der Dispersoidchemie" (1911); "Zur Lehre von den Zuständen der Materie" (1914).

particles as a result of diffusion. The velocity of condensation at the important first moment of the first stage of the process is formulated thus:

$$W = K \frac{\text{condensation pressure}}{\text{condensation resistance}} = K \frac{Q - L}{L} = K \frac{P}{L} = KU \quad (1)$$

in which W is the initial rate of precipitation, K a constant, Q the total concentration of the substance that is to precipitate, L the solubility of coarse crystals of the substance, $Q - L = P$, the amount of supersaturation. The ratio $\frac{P}{L} = U$, is the percentage supersaturation at the moment precipitation begins. To take care of other factors which may enter into the process, von Weimarn introduces a "variable multiplier" J and the equation becomes:

$$W = KJ \frac{Q - L}{L} \quad (2)$$

The velocity of the second stage of the process is given by the Nernst-Noyes equation:

$$V = \frac{D}{S} \cdot O \cdot (C - l) \quad (3)$$

where D is the diffusion coefficient, S the thickness of the adherent film, O the surface, C the concentration of the surrounding solution, and l the solubility of the disperse phase for a given degree of dispersity. $C - l$ may be termed the absolute supersaturation.

By the aid of these equations, several facts are interpreted. It will be seen that the velocity of precipitation depends not on the supersaturation P , but on the percentage supersaturation $\frac{P}{L}$. Thus, with a given value of P (say, a few grams per 100 cubic centimeters), a very soluble substance, such as sodium chloride, will deposit nothing at first and finally a few crystals may form; but with the same value of P , an almost insoluble substance, such as alumina or silver chloride, will give an immediate gelatinous or curdy precipitate. The difference is, that the velocity of precipitation is much smaller in the first case than in the second. On the other hand, if sodium chloride is formed by the interaction of sodium ethylate or sodium thiocyanate and hydrochloric acid in a mixture of ether and amyl alcohol, in

which sodium chloride is practically insoluble, the precipitate is curdy like that of silver chloride.

While the value of P is not in itself of primary importance in determining the form of a precipitate, its value is not without influence, since quite different results are obtained, depending on whether a given value of U is obtained by a large P or by a small L . In the first case a large amount of disperse phase must be produced, and in the second very little. Hence, if U is large, the former will, in general, give a gelatinous precipitate or jelly, and the latter a larger number of highly dispersed particles—a sol.

Von Weimarn considers that, with increasing supersaturation, five stages can be distinguished in the case of sparingly soluble substances, although the dividing line between the stages is not sharp. If the supersaturation is slight, no precipitation occurs inside of several years; in the next stage of higher supersaturation, perfect crystals appear in a relatively short time; in the third stage, skeleton crystals and needles are obtained; and in the highest stage of supersaturation, a jelly results. Von Weimarn believes all precipitates to be crystalline; but he believes gases and liquids to be crystalline, which is conclusive evidence that he is not restricting the term crystalline to its ordinary use.

Von Weimarn has tested his theory in a large number of cases and he claims that it interprets the facts quantitatively in every instance. While this claim seems to be altogether too extravagant in the light of the facts to be recounted later, certain points in his theory have quite general validity. The case of barium sulfate will serve to illustrate his observations. The solubility of this salt (0.0024 gram per liter at 18°) is fairly high compared to that of hydrous alumina, say; hence with ordinary laboratory solutions of barium chloride or nitrate and alkali sulfates, the values of P which can be obtained are not large enough to give large values of U . Under these conditions, the rate of formation of particles is relatively slow and their subsequent growth is rapid. Accordingly, the precipitate ordinarily obtained is made up of fairly large crystals. But by making use of more soluble salts, such as barium thiocyanate or iodide and ammonium or manganese sulfate, it is possible to obtain the salt in any form from large crystals to a clear jelly. In the actual experiments, equivalent solutions are mixed in equal volumes. Obviously, it is

necessary to use correspondingly large volumes of the very dilute solutions, otherwise there will not be a visible quantity of barium sulfate to separate out. Strictly, the product of the volume and concentration should be a constant.¹ The results of a series of observations are summarized in Table I.

TABLE I.—EFFECT OF THE CONCENTRATION OF REAGENTS ON THE PHYSICAL CHARACTER OF BARIUM SULFATE

Normality of reagents $\text{Ba}(\text{CNS})_2$ and MnSO_4	P Excess of BaSO_4 , grams per 100 cubic centimeters	$U = \frac{P}{L}$ $L = 0.0002$ gram in 100 cubic centimeters	Nature of precipitate
0.00005 to 0.00014	0.0000 to 0.0006	0 to 3	No precipitate in a year. Microcrystals to be expected in a few years and macro- crystals from very large amounts of solution
0.00014 to 0.0017	0.0006 to 0.0096	3 to 48	Slow precipitation at $U = 8$. Momentary solstage at $U =$ 25. Complete separation in months to hours
0.0017 to 0.75	0.0096 to 4.38	48 to 21,900	Precipitation in few seconds at $U = 48$; beyond this, instant- aneous precipitation of crys- tal skeletons and needles; at $U = 21,900$, crystals are barely recognizable
0.75 to 3.0	4.38 to 17.51	21,900 to 87,500	Immediate formation of appar- ently amorphous precipitates
3.0 to 7.0	17.51 to 40.90	87,500 to 204,500	Cellular clear jellies

From the above data it is obvious that a sol of barium sulfate cannot be obtained unless L is diminished, since increasing P

¹ VON WEIMARN: "Zur Lehre von den Zuständen der Materie," 83 (1914).

leads to the formation of a jelly. A sol can be formed by the addition of alcohol to the water as Kato¹ has demonstrated.

Von Weimarn recognized that the velocity W of the first stage of precipitation cannot be measured in actual practice, and that, in many cases especially interesting in the synthesis of colloid systems, the velocity U of the growth of particles cannot be determined. In due time, therefore, he introduced a specific coefficient called the "precipitate form coefficient" or "dispersity coefficient" N which is given by the expression:

$$N = \frac{P}{L} \cdot K_{ab} \cdot K_{cd} \cdot K_{ba} \cdot K_{ac} \cdot Z \quad (4)$$

in which $\frac{P}{L}$ is the percentage supersaturation as in the velocity equation, Z the viscosity, and K_{ab} , K_{cd} , etc. represent the "physical and chemical association" of the substances AB , CD , etc., which enter into the reaction AB (in solution) + CD (in solution) = AC (precipitate) + BD (in solution). The significance of "physical association" is known but it is not clear what von Weimarn means by "chemical association." This makes no difference, however, for the several factors are neglected and N is set down equal to $\frac{P}{L}$, that is,

$$N = \frac{P}{L} \quad (5)$$

or better,

$$N = J^P \quad (6)$$

in which J has the same significance as in Eq. (2).

Now if N is taken as approximately equal to $\frac{P}{L}$ as von Weimarn first assumed, then for the different substances x , y , and z ,

$$N_x = \frac{P_x}{L_x}; N_y = \frac{P_y}{L_y}; \text{ and } N_z = \frac{P_z}{L_z}$$

If the character of the precipitate is to be the same, irrespective of the chemical nature of the salt; in other words, if

$$N_x = N_y = N_z$$

then

$$\frac{P_x}{L_x} = \frac{P_y}{L_y} = \frac{P_z}{L_z}. \quad (7)$$

¹ Mem. Coll. Sci., Kyoto Imp. Univ., 2, 187 (1909).

This is the simplest expression for von Weimarn's Law of Corresponding States for the Precipitation Process, which says that under corresponding conditions of precipitation, the mean magnitude (expressed in gram molecules) of the crystals of substances capable of precipitation, will be the same. In the form given in Eq. (7) the so-called law can hardly be regarded as a first approximation, even with substances that are related chemically. This is illustrated by the observations of Buchner and Kalff¹ recorded in Table II. L is the solubility of the several salts and N is calculated from the concentrations of the solutions employed

using the expression $N = \frac{P}{L}$.

TABLE II.—PHYSICAL STATE OF PRECIPITATES

Salt	L	N	State of precipitate
CaF_2	4×10^{-4}	3,400	Jelly
BaF_2	18×10^{-3}	75	Jelly
CaSO_4	3×10^{-2}	140	Jelly
BaSO_4	2×10^{-5}	100,000	Jelly
AgCl	1×10^{-5}	700,000	Colloidal, instable
AgBr	7×10^{-7}	8,000,000	Colloidal, instable
AgI	1.5×10^{-8}	30,000,000	Jelly, instable
PbI_2	4.8×10^{-3}	360	Colloidal

Considering the first four salts, it will be seen that the nature of the precipitate is the same although the value of N varies between 75 and 100,000. Von Weimarn obtained well defined crystals of barium sulfate at values of N varying between 50 and 20,000. The law of corresponding states in the simplest form would require that, under the conditions recorded in the table, CaSO_4 , CaF_2 , and BaF_2 should give crystalline precipitates instead of transparent jellies. Considering next the silver halides: If von Weimarn's law in its simplest form held, these salts should give jellies more stable than barium sulfate under the conditions used; but, instead, they form colloidal solutions which later come down in flocks of an entirely different physical char-

¹ *Rec. trav. chim.*, **39**, 135 (1920).

acter from the barium sulfate jelly. Finally, the small value of N for lead iodide would lead one to expect the formation of a definitely crystalline precipitate under the conditions employed; actually, a jelly results.

An even more striking exception to von Weimarn's theory is the case of manganese arsenate, which can be made to form a stiff jelly by mixing very dilute solutions of potassium arsenate and manganese sulfate.¹ The value of L for the precipitate is so large that precipitation is slow and quantitative precipitation impossible, so that $\frac{P}{L} = N$ is very small.

Von Weimarn's² explanation of these discrepancies is, of course, that the law of corresponding states for the precipitation process is not the simple expression

$$\frac{P_x}{L_x} = \frac{P_y}{L_y} = \frac{P_z}{L_z} \dots$$

but

$$J_x \cdot \frac{P_x}{L_x} = J_y \cdot \frac{P_y}{L_y} = J_z \cdot \frac{P_z}{L_z} \dots$$

in which J_x , J_y , and J_z are specific variable multipliers, the value for any substance being "the product of all other factors (in addition to $\frac{P}{L}$) which influences the crystallization process."

These values must be expressed by abstract numbers such that the values for $\frac{P}{L}$ are equivalent."³ In other words, von Weimarn's equation for his so-called law becomes quantitative and generally applicable by putting in "variable multipliers," handy wastebaskets, as it were, into which are thrown all the variable factors known or unknown which have not been evaluated.

While facts may be expressed fairly accurately by means of such flexible formulas, it is doubtful whether anything is gained scientifically by regarding formulations of this kind as quantitative representations of natural laws. Von Weimarn evidently thinks so, but his opinion is not shared generally. Thus, Bancroft⁴ prefers to discard the formulas altogether and state the

¹ WEISER and BLOXSON: *J. Phys. Chem.*, **28**, 26 (1924); see p. 376.

² *Kolloidchem. Beihefte*, **18**, 48 (1923).

³ VON WEIMARN: *Kolloidchem. Beihefte*, **18**, 48 (1923).

⁴ *J. Phys. Chem.*, **24**, 100 (1920).

whole thing from another point of view. He points out that the mean size of the crystals is determined by the total amount of material crystallizing and the number of nuclei. The really important thing, therefore, is the number of nuclei which are formed under any given conditions. It is contended, very properly, that factors other than percentage supersaturation influence the number of nuclei formed. Thus the specific nature of the substance, stirring, and temperature have a profound effect on nuclei formation, and adsorption exerts a marked influence on the growth of particles.¹ Freundlich² likewise does not believe that the separation of a solid phase is generally and uniformly regulated by its solubility and the supersaturation prevailing: "What is known concerning the extraordinary sensitiveness to foreign substances of the velocities of formation of nuclei and crystallization makes it *a priori* improbable, and experience has not confirmed this theory."

Von Weimarn's reply is that all of the several specific factors other than $\frac{P}{L}$ are taken into account by means of his variable multiplier. It seems rather unfortunate for von Weimarn to conclude that criticism of his point of view is due largely to misunderstanding owing to incomplete knowledge of his work. What seems more likely is that people understand it too well and so refuse to recognize the general validity of a theory which is formulated by the use of a variable multiplier made up of an indefinite number of unevaluated factors.

In this connection, one seems justified in raising the question as to what is gained by substituting activities for concentrations in order to bridge the gap between actual and ideal solutions. Dawson³ writes:

The deviation of actual from ideal behavior may be conveniently expressed by the activity coefficient (γ = ratio of activity to concentration), which may be defined as the factor by which the concentrations must be multiplied in order to make the expressions for mass action and free energy applicable to actual as distinguished from ideal solutes.

¹ WEISER: *J. Phys. Chem.*, **21**, 314 (1917).

² "Kapillarchemie," 631 (1922).

³ "Annual Reports on the Progress of Chemistry," **21**, 24 (1924).

The so-called activities obtained in this way are the values which one must substitute in the formulas in order to make the formulas fit.¹ So long as people are satisfied to follow such a procedure there is little hope of improving formulas which are admittedly inadequate or they would not contain factors which may be made up of several unevaluated variables.

While the separation of a solid phase is not regulated generally and uniformly by its solubility and the supersaturation prevailing, it should be emphasized that certain statements of von Weimarn have quite general validity. Thus, when the reacting solutes are very dilute, the resulting solid precipitates in a definitely crystalline form. At low concentrations, the velocity of formation of nuclei is small and the few nuclei which do form grow so slowly at the cost of the solid present in weakly supersaturated solution, that large crystals result. Conversely, when the reacting solutions are very concentrated, jellies are formed consisting of drops of the liquid surrounded by the solid. The rate of formation of nuclei is extremely high at the high concentration, so that at any point where the two liquids touch there is formed immediately a feltwork of nuclei which do not have time to crystallize further and so yield a solid film, probably of amorphous character. Subsequently, the nuclei grow into crystals as the interacting substances diffuse through the film.²

Although, as von Weimarn points out, substances precipitated from solution pass through the colloidal state at some stage of the process, the problem of colloid synthesis is to create conditions such that this state is maintained for an indefinite period. The only thing the von Weimarn theory tells us is that negligibly small solubility and high dilution favor sol formation. The methods actually employed involve precipitation as finely divided particles and suitable strong adsorption, including protective colloids, or keeping the concentration of agglomerating agents low by choice of reaction or by dilution³. The most typical condensation reaction for the preparation of colloidal metals is reduction, for the preparation of colloidal hydrous oxides is

¹ BANCROFT: *J. Phys. Chem.*, **30**, 1194 (1926); Colloid Symposium Monograph, **4**, 29 (1926).

² Cf. FREUNDLICH: "Kapillarchemie," 631 (1922).

³ Cf. BANCROFT: *J. Phys. Chem.*, **18**, 556 (1914).

hydrolysis, and for the preparation of colloidal salts is metathesis. We shall list only the general methods of forming colloidal salts, together with some specific illustrations.

Metathesis in Which the Second Product is a Non-electrolyte.—The stability of a sol formed by metathesis depends to a great extent on the second product of the reaction. If the reaction is chosen so that the second product is a non-electrolyte, the conditions will be favorable to sol formation. The classic example under this heading is the action of hydrogen sulfide on a solution of arsenic trioxide: $\text{As}_2\text{O}_3 + 3\text{H}_2\text{S} = \text{As}_2\text{S}_3 + 3\text{H}_2\text{O}$.¹ The electrolyte concentration is quite low throughout the process and the salt remains dispersed as negatively charged particles stabilized by preferential adsorption of HS' ion. This sol can be made as concentrated as 3 grams As_2S_3 per 5 grams of water.² Similarly, the reaction between mercuric cyanide and hydrogen sulfide yields mercury sulfide which remains colloidal because of the small precipitating action of the slightly ionized prussic acid.³ Copper glycine treated in a similar way yields a copper sulfide sol.

Metathesis in Which the Second Product is an Electrolyte.—When an electrolyte is the second product of the decomposition, a stable sol will be obtained only in case the dilution is low or the electrolyte formed contains a strongly adsorbed ion. Thus, sols of the metallic sulfides are obtained by the interaction of very dilute solutions of the respective chlorides and hydrogen sulfide.⁴ Antimony trisulfide⁵ sol formed by the action of hydrogen sulfide on potassium antimony tartrate is stable even in fairly concentrated solution, owing to the presence of the strongly adsorbed tartrate ion. Lottermoser⁶ found that at sufficiently low concentrations, colloidal silver halides result from the interaction of silver nitrate and alkali halide, provided one or other of the reagents is in slight excess. With the silver salt in excess, the particles are positively charged by reason of preferential adsorption of silver ion; and with the halide in excess, the particles are negatively charged because of preferential adsorption of halide ion. Barium sulfate

¹ BERZELIUS: "Lehrbuch der Chemie," 3rd ed. (1834).

² SCHULZE: *J. prakt. Chem.*, [2], **25**, 431 (1882).

³ LOTTERMOSER: *J. prakt. Chem.*, [2] **75**, 293 (1907).

⁴ WINSSINGER: *Bull. soc. chim.*, [2] **49**, 452 (1888).

⁵ SCHULZE: *J. prakt. Chem.*, [2] **27**, 320 (1883).

⁶ *J. prakt. Chem.*, [2] **68**, 341 (1903); **72**, 35 (1905); **73**, 374 (1906).

precipitated from aqueous alcohol comes down as a gel which forms a clear sol on shaking with a larger quantity of water.¹ Strong adsorption of the alcohol doubtless helps to prevent coalescence or growth of the colloidal particles, since a jelly formed from aqueous solution does not form a stable sol on shaking with water.

Metathesis in the Presence of Strongly Adsorbed Substances. The precipitation of salts is frequently prevented from going beyond the colloidal stage in the presence of strongly adsorbed substances, such as the so-called protective colloids and sugar or glycerin. Thus, stable sols of the silver halides and Prussian blue are obtained by precipitation in the presence of gelatin.² Silver sulfide and cadmium sulfide are stabilized by gum arabic or casein.³ Silver chromate remains colloidal in the presence of an excess of sugar⁴ and most salts can be kept in colloidal solution by sodium protalbinate and lysalbinate, salts of somewhat hypothetical acids obtained by saponification of albumin.⁵ Sodium chloride formed by the interaction of sodium malonic ester and chloracetic ester in dry benzene is stabilized in the sol condition by strong adsorption of one or more of the organic reagents.⁶

Replacement of Solvent.—In this general method, which is of limited application in the preparation of colloidal salts, the solvent is replaced by a liquid in which the solute is insoluble and thus appears as a dispersed phase. Thus, if silver iodide is dissolved in potassium iodide and the solution poured into a large volume of water, a silver iodide sol results. The sol owes its stability to preferential adsorption of iodide ion.

Oxidation.—It is possible to prepare sols of certain colloidal salts by oxidation of colloidal solutions of the metals. Thus colloidal silver halides are obtained by the action of chlorine, bromine, and iodine on a sol of metallic silver.⁷

¹ KATO: *Mem. Coll. Sci., Kyoto Imp. Univ.*, **2**, 187 (1909).

² LOBRY DE BRUYN: *Rec. trav. chim.*, **19**, 236 (1900).

³ MÜLLER and ARTMANN: *Oesterr. Chem. Ztg.*, **7**, 149 (1904).

⁴ LOBRY DE BRUYN: *Ber.*, **35**, 3079 (1902).

⁵ PAAL: *Ber.*, **39**, 1436 (1906); PAAL and KÜHN: *Ibid.*, **39**, 2859, 2863 (1906); **41**, 51, 58 (1908).

⁶ MICHAEL: *Ber.*, **38**, 3217 (1905).

⁷ LOTTERMOSER and MEYER: *J. prakt. Chem.*, [2] **56**, 247 (1897); **57**, 543 (1898).

DISPERSION METHODS

Dispersion methods of preparing colloidal solutions involve the washing out of precipitating agents, the addition of peptizing agents, and disintegration by electrical or other means. Each of these general methods has been employed in the formation of colloidal salts.

Washing Out of Precipitating Agent.—When a precipitate consists of finely divided primary colloidal particles that have agglomerated into aggregates sufficiently large to settle, it may be repeptized by washing out the electrolyte that is responsible for the agglomeration. This method is particularly successful in the formation of colloidal hydrous oxides and it is applicable to the preparation of certain colloidal salts. Thus zinc sulfide thrown down from chloride solution by ammonia is peptized in part by washing out the ammonium salt.¹ Colloidal copper ferrocyanide precipitated from alkali ferrocyanide solution with excess copper salt is peptized if the copper salt is removed by washing.² Silver halides thrown down rapidly and washed at once by decantation are peptized in part. For the method to be successful, it is essential that the primary particles of the precipitate should be of colloidal dimensions and that they should not grow by a process of recrystallization by solution of the smaller grains and growth of larger ones at their expense (Ostwald ripening).

Addition of Peptizing Agent.—If the primary particles have grown to such an extent that the coagulation is irreversible by washing out the precipitating agent, the desired results may be obtained by the addition of a suitable peptizing agent. Thus, Prussian blue gel is peptized by oxalic acid and freshly precipitated metallic sulfides are peptized by hydrogen sulfide. Carbon dioxide passed into a solution of barium oxide in methyl alcohol gives a thick gel of barium carbonate. On the addition of more gas the gel is peptized, forming an opalescent sol.³

Electrical Disintegration.—The formation of sols by means of an electric arc under water or organic liquids is applicable chiefly

¹ DONNINI: *J. Chem. Soc.*, **66** (2), 318 (1894).

² BERKELEY and HARTLEY: *Phil. Trans.*, **206A**, 486 (1906).

³ NEUBERG and NEIMANN: *Biochem. Z.*, **1**, 166 (1906); NEUBERG and REWALD: *Kolloid-Z.*, **2**, 321 (1908).

to the preparation of metallic sols, but the method may be used also in preparing certain colloidal salts which conduct the current fairly well. Thus, von Hahn¹ obtained stable sols of galena, molybdenite, and antimonite² by cathodic disintegration with the direct-current arc.³ The dispersion of molybdenite takes place only when the temperature exceeds 53° more or less, the critical temperature being slightly different with different minerals. This is the first case recorded of a critical temperature in electrical synthesis of sols. The oscillatory discharge⁴ gives sols with antimonite, sphalerite, chalcocite, and molybdenite, while only coarsely dispersed systems are obtained with iron pyrites and molybdenite.

The general methods of formation of the colloidal salts having been outlined, attention will be directed toward a detailed consideration of the colloid chemistry of this class of inorganic substances. It seems advisable to begin with the colloidal sulfides, since the readily prepared sol of arsenic trisulfide has been used more often than any other colloidal salt in the investigation of colloid chemical phenomena.

¹ *Kolloid-Z.* (Zsigmondy Festschrift) **36**, 277 (1925).

² Cf. CURRIE: *J. Phys. Chem.*, **30**, 205 (1926).

³ BREDIG: *Z. Elektrochem.*, **4**, 514 (1898); BREDIG and BERNECK: *Z. physik. Chem.*, **31**, 258 (1899).

⁴ SVEDBERG: *Ber.*, **38**, 3616 (1905); **39**, 1705 (1906); *Kolloid-Z.*, **2**, Supplement 2 (1908).

I
COLLOIDAL SULFIDES

CHAPTER II

COLLOIDAL ARSENIC TRISULFIDE

Arsenic trisulfide is precipitated as a citron-yellow gel by passing hydrogen sulfide into a solution of arsenic trioxide acidified with hydrochloric acid. Spring¹ claims to get a hydrate, $\text{As}_2\text{S}_3 \cdot 6\text{H}_2\text{O}$, on drying the gel at room temperature in a current of air having a relative humidity of 70 per cent. The specified volume of the alleged hydrate is greater than that of the sum of the constituents; hence water is removed by applying pressure. It is unlikely that the product is other than amorphous arsenic trisulfide with adsorbed water, the composition of which can be varied continuously by changing the conditions of drying. X-radiograms of the freshly precipitated and of the aged sulfide show no interference rings, indicating the absence of a definite crystalline structure.² The colloidal character of the precipitated sulfide is further evidenced by the fact that the freshly formed gel is decomposed appreciably by water, giving hydrogen sulfide and arsenious acid, whereas the sulfide previously heated to 125° is more stable.³ When carried out carefully, the estimation of arsenic as arsenic trisulfide can be done with quantitative accuracy⁴ but Schmidt⁵ claims that the precipitate contains small amounts of both $\text{As}(\text{SH})_3$ and As_2O_3 , the respective errors being in the opposite direction and so equalizing each other.

The gel of arsenic trisulfide is distinctly yellow, but it usually assumes a redder color on drying. What has been termed a red allotropic modification⁶ is said to form by freezing or evaporating

¹ *Z. anorg. Chem.*, **10**, 185 (1895).

² HABER: *Ber.*, **55B**, 1717 (1922).

³ CLERMONT and FROMMEL: *Compt. rend.*, **87**, 330 (1879); CHODOUNSKY: *Chem. Zentr.*, I, 569 (1889); cf. CROSS and HIGGIN: *Ber.*, **16**, 1195 (1883).

⁴ PULLER: *J. Chem. Soc.*, **24**, 586 (1871); FRIEDHEIM and MICHAELIS: *Z. anal. Chem.*, **34**, 505 (1895).

⁵ *Arch. Pharm.*, **255**, 45 (1917); *Chem. Abstr.*, **11**, 3005 (1917).

⁶ WINTER: *Z. anorg. Chem.*, **43**, 228 (1905).

the sol and by precipitating the sol with a salt or acid followed by drying.¹ Durham² failed to obtain a red sulfide by any of these methods. A pure sol precipitates on freezing, giving a yellow gel. Drying the precipitate obtained from a sol by evaporation or by adding an alkali salt, gives an orange color. The sulfide formed by precipitating the sol with barium chloride possesses a brick-red color which Semler³ attributes to contamination by barium thioarsenite. Bhatnagar and Rao⁴ claim that the red color is due to the presence of some disulfide formed in accord with the reaction, $\text{As}_2\text{S}_3 + \text{H}_2\text{O} \rightarrow \text{As}_2\text{S}_2 \cdot \text{H}_2\text{S} + \text{O}$.

Bikerman⁵ obtained a red precipitate by prolonged boiling of a yellow arsenic trisulfide organosol in nitrobenzene. Merely heating the sol above 100° changed it to red, the yellow color returning at a lower temperature with no definite point of transformation. It is obvious that in a non-aqueous medium, As_2S_2 could not be formed in accord with the scheme of Bhatnagar and Rao nor could a red thioarsenite form in the absence of both metal and hydrogen ion. It seems quite probable that the change in color from yellow through orange to red is due, for the most part, to agglomeration of particles into denser aggregates, rather than to allotropy or to the presence of some impurity, although the latter may modify the color under certain circumstances.

PREPARATION AND GENERAL PROPERTIES OF ARSENIC TRISULFIDE SOL

Preparation.—Almost a century ago Berzelius⁶ called attention to the formation of a yellow solution when hydrogen sulfide is passed into a pure aqueous solution of arsenious acid. Since arsenic trisulfide precipitated out slowly, Berzelius suggested that the apparent solution was probably a suspension of transparent particles. The colloidal nature of the yellow liquid was

¹ GMELIN-KRAUT: "Handbuch anorg. Chem.," 7th ed., **3**, 219.

² Unpublished results.

³ *Kolloid-Z.*, **34**, 209 (1924).

⁴ *Kolloid-Z.*, **33**, 159 (1923).

⁵ *Z. physik. Chem.*, **115**, 261 (1925).

⁶ "Lehrbuch der Chemie," 3rd ed., **3**, 65 (1834); cf. GRAHAM OTTO: "Lehrbuch der Chemie," **2**, 863 (1840).

first definitely recognized by Schulze¹ who prepared stable sols of widely varying concentrations by passing hydrogen sulfide into arsenious acid solution and removing the excess hydrogen sulfide by boiling or by washing with hydrogen. The limiting concentration of sol obtained in this way is not determined by the solubility of arsenic trioxide in water. Thus Schulze prepared a sol containing 37.5 per cent As_2S_3 by adding small amounts of arsenic trioxide intermittently to a sol into which hydrogen sulfide was bubbled continuously. Picton² prepared a sol containing 5 grams of As_2S_3 per liter by dissolving arsenic trioxide in a solution of potassium acid tartrate or of sodium hydroxide before adding hydrogen sulfide and then purifying by dialysis.

As would be expected, the sols prepared under different conditions contain particles of widely varying sizes.³ In a quantitative study of the effect of conditions of sol formation on particle size, Boutaric and Vuillaume⁴ found the particle size to be larger the greater the concentration of arsenic trioxide, the higher the temperature, the slower the current of hydrogen sulfide, and the larger the excess of hydrogen sulfide. Most of the modifications in Schulze's procedure have been made with the end in view of obtaining stable sols containing particles of uniform size. Better results are obtained by allowing a dilute solution of arsenic trioxide to drop at a slow uniform rate into hydrogen sulfide water through which the gas is bubbled continuously.⁵ The most satisfactory procedure has been worked out by Freundlich and Nathansohn:⁶ 50 to 100 cubic centimeters of a cold saturated solution of arsenious acid are diluted to 200 cubic centimeters and mixed with 100 cubic centimeters of a solution containing 1 cubic centimeter of a saturated solution of hydrogen sulfide. After a light-yellow coloration appears, the mixture is diluted to 1 liter with a hydrogen sulfide solution ten times as strong as the above. Finally, the solution is saturated with the

¹ *J. prakt. Chem.*, [2] **25**, 431 (1882).

² *J. Chem. Soc.*, **61**, 137 (1892.)

³ PICTON: *J. Chem. Soc.*, **61**, 140 (1892); LINDER and PICTON: **67**, 63 (1895); BILTZ: *Nachr. königl. Ges. Wiss. Göttingen*, **2**, 1 (1906).

⁴ *Compt. rend.*, **178**, 938 (1924).

⁵ LINDER and PICTON: *J. Chem. Soc.*, **67**, 63 (1895); KRUYT and VAN DER SPEK: *Kolloid-Z.*, **25**, 1 (1919).

⁶ *Kolloid-Z.*, **28**, 258 (1921).

gas, the excess being washed out with hydrogen. The sol gives a faint light cone in the ultramicroscope but there are no ultra-microns. The success of this method of preparing the sol is probably due to the fact that high concentrations of the reacting solutions are avoided and the saturation with hydrogen sulfide is delayed until there is present a large number of arsenic trisulfide nuclei.

On account of the very low solubility of arsenic trisulfide (2.1×10^{-6} mols per liter)¹ the transformation to the sol state is quantitative in the presence of a slight excess of hydrogen sulfide.² Since the salt hydrolyzes to a certain extent, washing the sol with hydrogen for too long a time results in some decomposition, hydrogen sulfide being carried off and a corresponding amount of arsenious acid remaining in solution.

On mixing 5 cubic centimeters of $N/10$ H_3AsO_3 with 5 to 10 cubic centimeters of $N/100$ H_2S in 300 cubic centimeters of pure water, there results a clear solution which turns yellow suddenly after a few seconds. If diluted still more, the solution will remain colorless in the dark for several days, although a trace of dilute acids causes it to turn yellow immediately. Since the removal of hydrogen sulfide from the colorless solution with a stream of hydrogen takes place very slowly, Vorländer and Häberle³ conclude that hydrogen sulfide and arsenious acid react in very dilute solution forming an instable molecular compound which is hydrolyzed to a certain extent into the original substances. Semler⁴ suggests that this compound may be thio-arsenious acid. Peskov⁵ makes the more probable assumption that the colorless solution contains ordinary arsenic trisulfide, the absence of color being due to two factors: the extremely small magnitude of the primary particles and, more especially, the complete individuality of the particles. Agglomeration of the fine particles into larger secondary aggregates which appear yellow is prevented in the colorless solution owing to the protecting effect of a relatively large excess of arsenious acid.

¹ WEIGEL: *Z. physik. Chem.*, **58**, 293 (1907).

² KÜSTER and DAHMER: *Z. anorg. Chem.*, **33**, 105 (1902); **34**, 410 (1903).

³ *Ber.*, **46**, 1612 (1913).

⁴ *Kolloid-Z.*, **34**, 213 (1924).

⁵ *J. Russ. Phys. Chem. Soc.*, **46**, 1619 (1914); *J. Chem. Soc.*, **108** (2), 429 (1915).

Color.—The color of arsenic trisulfide sol varies from red-orange to citron-yellow, depending on the size of the particles and the concentration. A sol with very small particles appears more orange than one of the same concentration containing large particles. A concentrated sol always appears yellower than a dilute one, probably because the former is likely to contain larger aggregates. Because of the marked opalescence and coloring power of the colloidal particles, one part of As_2S_3 in 100,000 parts of water can be detected in thin layers.

Boutaric and Vuillaume¹ studied the absorption spectrum of a sol by means of the Fèry spectrophotometer. Designating the intensity of the incident radiation λ by I_o and the intensity of the radiation after traversing the absorbing medium by I , then if the sol behaves as a turbid medium, $\log \frac{I_o}{I}$ should vary inversely as the fourth power of λ in accord with Rayleigh's law, where the suspended particles are small compared with λ ; and $\log \frac{I_o}{I}$ should vary inversely as some power n of λ for larger particles, n being less than 4 and correspondingly less as the particles are greater. The absorption curve of a sol containing 6.2 grams As_2S_3 per liter did not follow either of these laws but showed a regular increase in n from $n = 33$ for $\lambda = 6400$ to $n = 12$ for $\lambda = 5300$ with $n = 4$ at about $\lambda = 6200$. The absorption thus appears to be the resultant of two phenomena: an absorption by diffusion obeying Rayleigh's law, and a selective absorption caused by the reflection of incident rays from the surface of the particles. The latter absorption should vary with the extent of total surface, diminishing for a constant weight of the sulfide as the size of the particles is increased. In accord with this view, it was found that prolonged boiling, which increases the particle size, decreases the selective absorption.

Density and Viscosity.—The density of arsenic trisulfide sols varies linearly with the concentration² up to about 9 per cent, above which it increases more rapidly.³ For concentrations up to 3.6 per cent the index of refraction is also a linear function of

¹ *Compt. rend.*, **177**, 259 (1923).

² LINDER and PICTON: *J. Chem. Soc.*, **67**, 71 (1895); WINTGEN: *Kolloid-chem. Beihefte*, **7**, 266 (1915).

³ BOUTARIC and SIMONET: *Bull. acad. roy. méc. Belg.*, [5] **10**, 150 (1924).

the concentration. The refractive index is apparently independent of the degree of dispersion.¹

The density of the colloidal particles of arsenic trisulfide has been estimated by Dumanski² by applying Einstein's³ formula for the viscosity of suspensions of rigid spheres,

$$n = n_o(1 + kf) \quad (1)$$

where n is the viscosity of the sol, n_o the viscosity of the pure liquid, f the volume of the suspended particles and k a constant which Einstein at first took to be unity but which he later made equal to 2.5. From viscosity measurements, f can be determined and if the concentration of the suspended particles c is known, d the density of the particles follows from the expression,

$$d = \frac{c}{f} \quad (2)$$

Since the particles adsorb water, the value of c cannot be determined analytically. This is gotten indirectly from the density of the sol d_s , the density of the medium d_w , and f . Thus

$$d_s = d_w + c - \frac{c}{d}d_w \quad (3)$$

but since

$$\frac{c}{d} = f, \quad (2)$$

$$c = d_s - d_w + fd_w$$

Taking the value of k in Einstein's equation as unity, Dumanski finds the density of the particle of colloidal As_2S_3 to be 1.50 ± 0.02 . Later he makes $k = 2.5$ and so concludes that f , from Eq. (2), is 2.5 times larger than it should be, and so calculates d to be 3.75 ± 10 . Dumanski seems to have completely overlooked the fact that if f is 2.5 times larger than it should be in his original equation, this will change the calculated value of c also. Had he calculated d from Eqs. (1) ($k = 2.5$), (2), and (3), as he says he does, the value of d would come out to be 1.90. This value would appear to be much nearer correct than 3.75, since the particles with their adsorbed water must be less dense

¹ LIFSHITZ and BECK: *Kolloid-Z.*, **26**, 10 (1920).

² *Kolloid-Z.*, **12**, 6 (1913); **13**, 222 (1913); **9**, 262 (1911).

³ *Ann. Physik.*, [4] **19**, 289 (1906); **34**, 591 (1911); *Kolloid-Z.*, **27**, 137 (1920).

than the crystalline mass of As_2S_3 whose density is 3.45. There is, however, no reason to believe that density determinations involving the use of Einstein's equation are any more than first approximations, at best. As already mentioned, Einstein at first made $k = 1$ and later changed it to 2.5; Bancelin¹ found k to be 2.9 for a suspension of gamboge, and Hatschek² used $k = 4.5$. According to these formulas, the viscosity is independent of the degree of dispersion, which is not the case. Thus Odén³ found the viscosity of sulfur sols in which the particles have a diameter of $10\mu\mu$ to be 50 per cent greater than with sols in which the sulfur particles have a diameter of $100\mu\mu$. Hatschek⁴ attributes this to the presence of an adsorbed layer of water on the particles which increases the effective volume of the smaller particles much more than the larger ones. Boutaric⁵ finds the value of k to vary continuously with dilution approaching 2.5 as the dilution approaches infinity.

From the density of the sol and water, together with the concentration determined analytically, Dumanski calculates the density of the As_2S_3 in the particles from Eq. (3) above, to be 3.11.⁶ By a similar procedure Burton and Currie⁷ find the density of As_2S_3 in the colloidal state to be the same as the density in mass.

Chemical Action.—Ozone acts on arsenic trisulfide sol giving arsenic acid.⁸ Stannous chloride reduces it to As_2S_2 which is similar in color to Sb_2S_3 ; hence in qualitative analysis arsenic is sometimes mistaken for antimony in the presence of tin.⁹ Peskov¹⁰ studied the velocity of solution of colloidal arsenic trisulfide in sodium hydroxide or sodium carbonate and found the process to be subject to the lyotropic influence of the cations of neutral salts in the order: $\text{NH}_4 < \text{Li} < \text{Na} < \text{K} < \text{Rb} < \text{Cs}$.

¹ *Compt. rend.*, **152**, 1382 (1911).

² *Kolloid-Z.*, **7**, 301 (1910).

³ *Z. physik. Chem.*, **80**, 709 (1912).

⁴ *Kolloid-Z.*, **11**, 280 (1912).

⁵ BOUTARIC and VUILLAUME: *J. chim. phys.*, **21**, 247 (1924); BOUTARIC and SIMONET: *Bull. acad. roy. méd. Belg.*, [5] **10**, 150 (1924).

⁶ Cf. WINTGEN: *Kolloidchem. Beihefte*, **7**, 251 (1915).

⁷ *Trans. Roy. Soc. Can.*, **16**, III, 109 (1922).

⁸ RIESENFELD and HAASE: *Z. anorg. Chem.*, **147**, 188 (1925).

⁹ EHRENFELD: *Ber.*, **40**, 3962 (1907).

¹⁰ *Kolloid-Z.*, **32**, 163, 238 (1923).

The velocity of solution does not take place either as a purely heterogeneous or molecular process but appears to be a heterogeneous process modified by the large surface of the small particles and by Brownian movement.

If arsenic trisulfide sol is taken into the body in any way, it is precipitated in a granular form.¹ Injected intramuscularly or subcutaneously it appears in the tissues as minute granular particles. On intravenous injection, there is rapid coagulation which may result in small emboli in the capillaries, especially of the lungs. The sulfide produces a more marked pharmacological effect on the smallest lung capillaries and alveoli than any other organic or inorganic compound. Meneghetti suggests that for this reason non-lethal doses may have a therapeutic value in some diseases of the lungs. Traces of arsenic trisulfide sol have been found to increase liver autolysis but higher concentrations inhibit the process.²

Composition.—Linder and Picton³ are of the opinion that the colloidal sulfides are polymerized hydrosulfides such as $16\text{As}_2\text{S}_3 \cdot \text{H}_2\text{S}$, while Duclaux⁴ proposes the formula $(n\text{As}_2\text{S}_3 \cdot x\text{H}_2\text{S})$ as a basis for explaining coagulation by electrolytes as a purely chemical process. From the hydrogen ion content of an arsenic trisulfide sol, determined from its electrical conductivity and by electrometric titration with barium hydroxide, Pauli and Semler⁵ regard the sol as a quite strongly dissociated complex acid having the formula $[\text{xAs}_2\text{S}_3 \cdot \text{As}_2\text{S}_4\text{H}_2 \cdot \text{As}_2\text{S}_4\text{H}]' + \text{H}^-$. From similar measurements, Rabinovich⁶ arrives at the simpler formula $(\text{As}_2\text{S}_3)_x\text{HS}' + \text{H}^-$. Since the acidity of the filtrate after precipitation with BaCl_2 is greater than the sol, it is assumed that all the hydrogen is displaced by barium, giving an insoluble barium salt of the complex acid. As a matter of fact, every one knows that the composition of the sol varies with the method of

¹ MENEGHETTI: *Biochem. Z.*, **121**, 1 (1921); FOA and AGGazzOTTI: *Ibid.*, **19**, 1 (1909).

² ASCOLI and IZAR: *Biochem. Z.*, **6**, 192 (1907).

³ *J. Chem. Soc.*, **61**, 114 (1892).

⁴ "Les Colloïdes," Paris (1920).

⁵ *Kolloid-Z.*, **34**, 145 (1924); cf. BHATNAGAR and RAO: *Ibid.*, **33**, 159 (1923); DUCLAUX: *J. chim. phys.*, **6**, 592 (1908).

⁶ *Z. physik. Chem.*, **116**, 97 (1925); *J. Russ. Phys. Chem. Soc.*, **58**, 848 (1926).

preparation, the excess peptizing electrolyte, and the age; and it is not obvious what is gained by attempting to assign a formula to a mixture of variable composition.¹ Formed in the presence of hydrogen sulfide, the colloidal particles adsorb H₂S, H⁺ ions, and HS' ions in amount depending upon the physical character of the particles and the concentration of electrolyte. Now it is well known that a substance shows a strong tendency to adsorb closely related ions. In this case the adsorption of HS' is greater than that of H⁺ which gives the particles a negative charge. The excess of H⁺ ions in the intermicellar liquid is a measure of the excess of adsorbed HS' which gives the particles a charge. On the addition of BaCl₂ the strongly adsorbed Ba⁺⁺ ion not only neutralizes the excess HS' adsorption but displaces (exchange adsorption) the less strongly adsorbed H⁺ ion which goes into the filtrate, rendering the latter more acid than the intermicellar liquid. It should be pointed out that precipitated, dried, and powdered arsenic trisulfide adsorbs OH⁻ ion more strongly than H⁺ ion so that an acid solution is obtained by shaking a neutral salt with the powder.²

Action of Light.—Although an arsenic trisulfide sol is quite stable when first prepared, the stability decreases on standing, especially in the light. Thus Freundlich³ observed a decrease in concentration of approximately 15 per cent when a sol was allowed to stand for a year in a closed vessel. Dumanski⁴ placed a sol containing 65 grams per liter in a vessel 1 meter long and 2 centimeters in diameter, and observed the rate of fall of the particles. The velocity was approximately 0.031 centimeter per day over a period of 4 years. Since care was not taken to exclude light during the period of observation, it is probable that the settling was due indirectly to the agglomerating effect of light which resulted in the formation of particles sufficiently large to overbalance the effect of Brownian movement.

¹ WEISER: "The Hydrous Oxides," 52 (1926); cf. KPOACZEWSKI: Alexander's "Colloid Chemistry," 547 (1926).

² FREUNDLICH: *Z. physik. Chem.*, **73**, 396 (1910).

³ *Z. physik. Chem.*, **44**, 129 (1903).

⁴ *Kolloid-Z.*, **36**, 98 (1925).

The destabilizing action of light on arsenic trisulfide sol was first observed by Young and Pingree.¹ Freundlich and Nathansohn² attribute this to the photochemical oxidation of the hydrolysis product—hydrogen sulfide—to colloidal sulfur and pentathionic acid, accompanied by a reaction between the hydrogen sulfide and pentathionic acid which serve as the stabilizing electrolytes for arsenic trisulfide and sulfur, respectively.³ Removal of the stabilizing electrolytes in this way produces a decrease in the charge on the particles and the consequent precipitation. The electrical conductivity increases to a constant value on exposure to light, the rate of change increasing somewhat with diminishing concentration of sol. Murphy and Mathews⁴ attribute this to the building up of a concentration of the thionic acid sufficient to serve as the stabilizing electrolyte for the colloidal sulfur, the reaction between H_2S and thionic acid then proceeding at such a slow rate that equilibrium between the several components of the system is maintained and further change in the conductance is prevented. The rate of change of conductivity increases somewhat with diminishing concentration of electrolyte, probably owing to the increased photochemical activity of the sol per unit mass of arsenic trisulfide brought about by the greater dispersity of the more dilute sol.

ACTION OF ELECTROLYTES ON ARSENIC TRISULFIDE SOL

The Critical Coagulation Potential.—When electrolytes are added to a sol stabilized by the preferential adsorption of anions, precipitation takes place when there is sufficient cation adsorption to neutralize the combined adsorption of the original stabilizing ion and that added with the electrolyte in question. Actually the isoelectric point,⁵ the point of complete neutrality, need not be reached for Powis⁶ showed that reduction of the charge below a certain critical value will cause agglomeration. In Table III is given the potential difference at the surface of

¹ *J. Phys. Chem.*, **17**, 657 (1913); cf., also, BOUTARIC and MANIÈRE: *Bull. acad. roy. méd. Belg.* [5] **10**, 571 (1924).

² *Kolloid-Z.*, **28**, 258 (1921).

³ FREUNDLICH and SCHOLZ: *Kolloidechem. Beihefte*, **16**, 234 (1922).

⁴ *J. Am. Chem. Soc.*, **45**, 16 (1923).

⁵ HARDY: *Proc. Roy. Soc. (London)* **66**, 110 (1900).

⁶ *J. Chem. Soc.*, **109**, 734 (1916).

arsenic trisulfide particles when sufficient amounts of several electrolytes are added to cause fairly rapid agglomeration. The potential difference is the electrokinetic potential calculated from Freundlich's¹ equation,

$$\xi = \frac{4\pi\eta u}{HD}$$

where u is the migration velocity of the particles² moving under

TABLE III.—CRITICAL COAGULATION POTENTIAL OF COLLOIDAL PARTICLES IN As_2S_3 SOL

Electrolyte	Concentration milliequiva- lents per liter	Electrokinetic potential millivolts
KCl.....	40.0	44
BaCl ₂	1.0	26
AlCl ₃	0.15	25
Th(NO ₃) ₄	0.20	27
Th(NO ₃) ₄	0.28	26
Th(NO ₃) ₄	0.40	24

a potential H in a medium with a viscosity η and a dielectric constant D . It is significant that the critical potential is similar for all multivalent ions. Since the critical value at which potassium chloride is effective is greater than for the other electrolytes, Powis concludes that there is a salting-out effect with the relatively high concentration of potassium salt which causes coagulation when the calculated potential is higher. Kruyt³ has recently given a more probable explanation. Very careful measurements of the rate of cataphoresis u shows an increase on the addition of salts with univalent cations.⁴ This he attributes to change in the dielectric constant⁵ of the medium, especially with higher concentration of electrolytes. Hence, the calculated value of ξ for such electrolytes is higher than it should be. In

¹ "Kapillarchemie," 331 (1922).

² BURTON: *Phil. Mag.*, [6] 11, 425 (1906).

³ KRUYT, ROODVOETS, and VAN DER WILLIGEN: Colloid Symposium Monograph, 4, 304 (1926); IVANITSKAJA and PROSKURNIN: *Kolloid-Z.*, 39, 15 (1926).

⁴ Cf., however, FREUNDLICH and ZEH: *Z. physik. Chem.*, 114, 65 (1924).

⁵ WALDEN, ULLICH, and WERNER: *Z. physik. Chem.*, 116, 261 (1925); FÜRTH: *Physik. Z.*, 25, 676 (1924).

other words, the critical potential does not depend on a definite u value but on the value of $\frac{u}{D}$.

Although Powis succeeded in reversing the charge on the colloidal particles from negative to positive by means of thorium nitrate, he was unable to prepare a stable positive sol by the aid of this salt. Favorable conditions for reversal of charge on a sol would appear to be strong adsorption of the ion responsible for the reversal, very small particles, and a low coagulation velocity at the isoelectric point. The first condition is realized with thorium nitrate; but the last two conditions are not realized with a strong sol. Smoluchowski¹ showed the velocity of coagulation to decrease rapidly with diminishing concentration of particles which suggested that reversal could be realized with a very dilute sol. Freundlich and Buchler² succeeded in accomplishing this reversal with a sol containing 0.04 gram As₂S₃ per liter.

Velocity of Coagulation.—Smoluchowski³ developed a theory for the mechanism and velocity of the coagulation process in a sol made up of spherical particles after reducing the charge below the critical value. Under these circumstances, it is assumed that a sphere of attraction exists around each particle such that any other particle entering this sphere will be held. The radius of the sphere of attraction must be greater than twice the radius of the single particle. Two primary particles may become attached, whereupon the double particle can attract another primary particle giving a triple particle, etc. Smoluchowski first calculated the decrease in the number of primary particles which are brought into the sphere of influence of particles at rest by means of the Brownian movement. This was then extended to include a large number of particles which are in molecular motion. In the same way he calculated the decrease in the number of double and triple particles, finding that their number increases at first since they are formed by the collision of primary particles.

From such considerations, Smoluchowski arrived at the conclusion that the decrease in the total number of particles

¹ *Z. physik. Chem.*, **92**, 129 (1917).

² *Kolloid-Z.*, **32**, 305 (1923); MUKHERJEE and ROY: *J. Chem. Soc.*, **125**, 476 (1924).

³ *Z. physik. Chem.*, **92**, 129 (1917).

with the time takes place in accord with a reaction of the second order:

$$k = 4\pi DR = \frac{1}{t} \left(\frac{1}{\Sigma n} - \frac{1}{n_o} \right)$$

where k is the velocity constant, R the radius of the sphere of attraction, D the diffusion coefficient, n_o the total number of primary particles at the outset and Σn the total number of all kinds of particles after the time t . Solving for Σn

$$\Sigma n = \frac{n_o}{1 + kn_o t}$$

In a bimolecular reaction, T (the specific coagulation time) varies inversely as the concentration of particles at the start, i.e., $T = \frac{1}{kn_o}$, hence,

$$\Sigma n = \frac{n_o}{1 + \frac{t}{T}}$$

Since

$$\Sigma n = n_1 + n_2 + \dots + n_n$$

where n_1 is the number of single particles, n_2 of double particles, etc., then

$$n_1 = \frac{n_o}{\left(1 + \frac{t}{T}\right)^2}$$

$$n_2 = \frac{\frac{n_o}{T} \frac{t}{T}}{\left(1 + \frac{t}{T}\right)^3}$$

or

$$n_n = \frac{n_o \left(\frac{t}{T}\right)^{k-1}}{\left(1 + \frac{t}{T}\right)^{k+1}}$$

If the relative times $\frac{t}{T}$ are plotted against the relative number of particles $\frac{n}{n_o}$, a diagram (Fig. 1) is obtained which shows how the total number of particles Σn , the number of primary particles

n_o , etc. vary with the time. In accord with the equations, the total number of particles is reduced to one-half its value in the time T , while the number of primary particles is reduced to one-fourth in the same time; the curve for double particles has a maximum equal to $\frac{1}{2}n_o$ at the time $\frac{T}{2}$, etc. When the particles

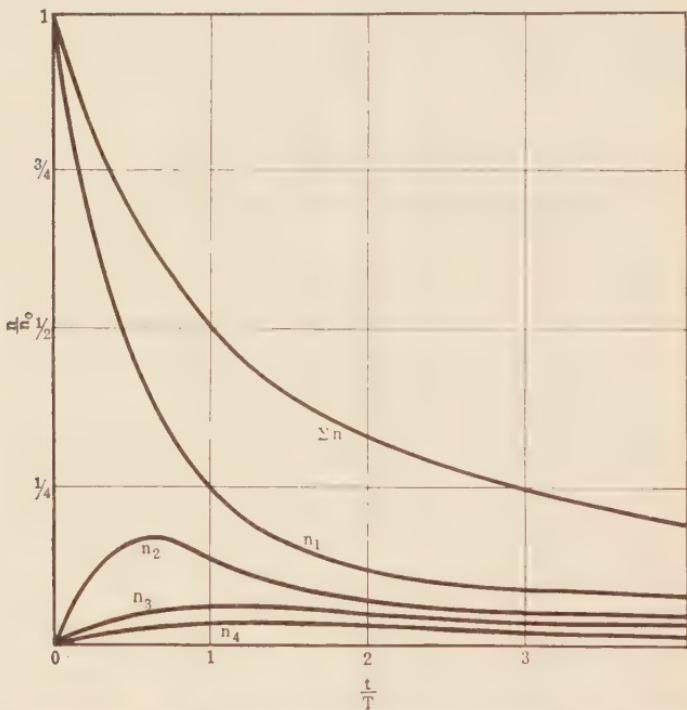


FIG. 1.—Variation in the relative number of particles during coagulation of sol.

are not discharged completely, only a portion of the collisions result in coalescence and we have what is called "slow" coagulation. Freundlich¹ assumes a constant force of attraction between particles for a given concentration of electrolyte below that required for rapid coagulation, but, because of repulsion, only those collisions are inelastic in which the particles collide with sufficient force. From this point of view, the greater the charge on the particles the greater must be the velocity of collision in

¹ *Kolloid-Z.*, **23**, 163 (1918); cf. KRUYT and VAN ARKEL: *Ibid.*, **32**, 29 (1923).

order to overcome the repulsive effect and so to bring about coalescence and agglomeration.

Mukherjee and Majumdar¹ followed the velocity of slow coagulation of arsenic trisulfide sol, using a spectrophotometer. Smoluchowski's theory was found to apply only in the initial stages of the coagulation process, a limiting stage of coalescence being ultimately reached where the equations failed completely. This stage was reached more rapidly with lower concentrations, that is, the slower the coagulation rate. The results were explained by assuming, as Freundlich does, that the coalescence is reversible or irreversible according to the magnitude of the ζ -potential of the particles. At sufficiently low concentrations of electrolyte it is reversible, but is irreversible at higher concentrations when the ζ -potential is small. The limiting stage results when there is an equilibrium between the rates of breaking up of the aggregates and of coalescence. From similar experiments on arsenic trisulfide sol, using potassium chloride as precipitating electrolyte, Jableczynski² obtained results for slow coagulation in good agreement with Smoluchowski's theory, provided the sol was not freed from hydrogen sulfide. Since Jableczynski furnishes the only examples of slow coagulation where the theory seems to hold, his observations should be confirmed. In this connection, it should be pointed out that Mukherjee eliminated the relation between intensity of light and size of particles in his observations, whereas Jableczynski introduced Lord Rayleigh's³ relation which Mie⁴ has found to be inapplicable.

Precipitation Values of Electrolytes.—Several methods have been employed from time to time for determining the relative precipitating power of electrolytes. Since the process is transitory, it is necessary to compare the electrolyte concentrations which produce the same velocity of coagulation. The rate of coagulation has been followed by means of viscosity measurements on alumina sol,⁵ by colorimetric observations on gold sol⁶

¹ *J. Chem. Soc.*, **125**, 785 (1924).

² *Bull. soc. chim.*, **35**, 1277 (1924).

³ *Phil. Mag.*, **41**, 107, 274, 447 (1874).

⁴ *Ann. Physik*, [4] **25**, 377 (1908); BOUTARIC and VUILLAUME: *Compt. rend.*, **177**, 259 (1923); see p. 21.

⁵ GANN: *Kolloidchem. Beihefte*, **8**, 64 (1916).

⁶ HATSCHEK: *Trans. Faraday Soc.*, **17**, 499 (1921).

and Congo rubin sol,¹ and with a spectrophotometer on gold sol and arsenic trisulfide sol.² For the most part, however, investigators compare the concentrations which just cause complete precipitation in a definite period of time, not less than 2 hours. As Freundlich³ has shown, these precipitation values have a definite meaning from the standpoint of coagulation since with certain concentrations there always exists a constant maximum coagulation velocity, the velocity of so-called instantaneous coagulation⁴ and hence the coagulations are comparable when this velocity is attained. Some observations of Freundlich⁵ on the precipitation of arsenic trisulfide sol are given in Table IV.

TABLE IV.—PRECIPITATION VALUES OF ELECTROLYTES FOR ARSENIC TRISULFIDE SOL

Electrolyte	Precipitation value, milliequivalents per liter	Electrolyte	Precipitation value, milliequivalents per liter
KC ₂ H ₃ O ₂	110.0	Morphine chloride....	0.425
LiCl.....	58.4	New fuchsine.....	0.114
NaCl.....	51.0	MgCl ₂	1.434
KNO ₃	50.0	MgSO ₄	1.620
KCl.....	49.5	CaCl ₂	1.298
K ₂ SO ₄	65.6	SrCl ₂	1.270
NH ₄ Cl.....	42.3	BaCl ₂	1.382
HCl.....	30.8	ZnCl ₂	1.370
H ₂ SO ₄	30.1	UO ₂ (NO ₃) ₂	1.284
Guanadine nitrate....	16.4	AlCl ₃	0.279
Strychnine nitrate....	8.0	Al(NO ₃) ₃	0.285
Aniline chloride.....	2.52	Ce ₂ (SO ₄) ₃	0.276

Except for the univalent organic ions, the salts with ions of the same valence fall in fairly well-defined groups, the univalent ions precipitating in highest concentration and the trivalent ions in

¹ LÜERS: *Kolloid-Z.*, **27**, 123 (1920).

² MUKHERJEE and MAJUMDAR: *J. Chem. Soc.*, **125**, 785 (1924); BOUTARIC and VUILLAUME: *Compt. rend.*, **172**, 1293 (1921).

³ *Kolloid-Z.*, **23**, 163 (1918).

⁴ SMOLUCHOWSKI: *Z. physik. Chem.*, **92**, 129 (1917).

⁵ *Z. physik. Chem.*, **73**, 385 (1910); cf., also, SCHILOW: *Ibid.*, **100**, 425 (1922); BACH: *J. chin. phys.*, **18**, 46 (1920).

lowest concentration, in accord with the so-called Schulze law.¹ It should be emphasized, however, that ions of the same valence do not behave alike and that the behavior of the alkaloid and dye cations follows no rule as to valence. Although the exceptions to Schulze's law are so numerous that it should be looked upon merely as a qualitative rule, Freundlich and Schucht² have used the principle with some success in confirming the valence of certain ions. Thus the results recorded in Table V indicate the trivalence of the rare earths and of indium. In a similar way, Galecki³ showed that beryllium behaved like a divalent

TABLE V.—PRECIPITATION VALUES OF SOME LESS COMMON ELECTROLYTES FOR ARSENIC TRISULFIDE SOL

Electrolytes	Precipitation value, milliequivalents per liter	Valence of cation
Strontium nitrate.....	1.08	2
Xantho cobalt sulfate.....	1.10	2
Purpureo cobalt chloride.....	1.10	2
Aluminum sulfate.....	0.225	3
Yttrium chloride.....	0.219	3
Cerium nitrate	0.225	3
Neodymium ammonium nitrate	0.240	3
Praseodymium ammonium nitrate.....	0.237	3
Samarium chloride.....	0.249	3
Europium chloride.....	0.276	3
Gadolinium chloride.....	0.240	3
Dysprosium chloride.....	0.258	3
Erbium chloride.....	0.192	3
Indium nitrate.....	0.246	3
Luteo cobalt chloride.....	0.246	3
Roseo cobalt chloride.....	0.360	3

metal as we now know that it should. The similarity in precipitating power of multivalent elements having the same charge is more striking in Table V than in Table IV, probably because the rare earth elements are quite similar and so are adsorbed

¹ SCHULZE: *J. prakt. Chem.*, [2] **25**, 431; **27**, 320 (1883).

² Z. physik. Chem., **80**, 564 (1912).

³ Z. Elektrochem., **14**, 767 (1908).

to about the same extent. Burton and Bishop¹ report that ceric nitrate behaves like a salt with a trivalent cation and not like one with a tetravalent cation. Since $\text{Ce}(\text{NO}_3)_4$ is said to be non-existent, it is probable that they were using the trivalent salt which is sometimes erroneously called ceric nitrate. It is interesting that the slow transformation of divalent purpureo cobalt chloride to the trivalent roseo salt can be followed by the gradual increase in precipitating power.

From investigations on the coagulation of arsenic trisulfide sol by different amine salts, Freundlich and Birstein² found the precipitating power to increase regularly with the addition of CH_2 groups in accord with Traube's rule which states that the capillary activity, that is, the lowering of the surface tension of water and the adsorption by solid adsorbents, increases regularly with the addition of CH_2 groups in an homologous series. This is illustrated by the data in Table VI. The addition of each successive pair of CH_2 groups causes a marked falling off in the

TABLE VI.—PRECIPITATION VALUES OF AMINES FOR ARSENIC TRISULFIDE SOL

Electrolyte	Precipitation value x , in milliequivalents per liter	Activity factor $\frac{x_n}{x_{n+1}}$
$\text{NH}_3 \cdot \text{HCl}$	35.00	
$\text{C}_2\text{H}_5\text{NH}_2 \cdot \text{HCl}$	18.20	1.9
$(\text{C}_2\text{H}_5)_2\text{NH} \cdot \text{HCl}$	9.96	1.8
$(\text{C}_2\text{H}_5)_3\text{N} \cdot \text{HCl}$	2.78	3.5
$(\text{C}_2\text{H}_5)_4\text{NCl}$	0.89	3.2

precipitation value of the salts. This decrease is, however, not directly proportional to the number of CH_2 groups as evidenced by the lack of constancy in the ratio recorded in the last column of the table. Similar observations were made on a hydrous ferric oxide sol with a series of sodium salts of the fatty acids. Moreover, the difficultly soluble sodium fumarate was found to

¹ *J. Phys. Chem.*, **24**, 701 (1920).

² *Kolloidchem. Beihefte*, **22**, 95 (1926).

have a much higher coagulating power than the more readily soluble isomeric sodium malonate. This is in accord with the usual view that the least soluble substance is the most capillary active, that is, the most strongly adsorbed.

While it is generally assumed that one is justified in neglecting the effect of anions in the precipitation of a negative sol by electrolytes and of cations in the precipitation of a positive sol,¹ it is evident that this will be true only in case the adsorption of the ion having the same charge as the sol is negligible either because of its nature or the dilution. While the effect may be slight in certain cases, it is quite marked in others, as illustrated by the results recorded in Table VII.

TABLE VII.—PRECIPITATION VALUES OF POTASSIUM SALTS FOR ARSENIC TRISULFIDE SOL

Concentration of sol, grams per liter.....		1.8	3.7	6.0
Precipitation value of	KCl	49.5	85	33.2
	K ₂ SO ₄	65.6	100	43.5
	K ₄ Fe(CN) ₆	185	71.2
	K ₂ (C ₄ H ₄ O ₆)	240.0	270	
Investigator.....	Freundlich ¹	Ghosh and Dhar ²	Weiser and Nicholas ³	

¹ Z. physik. Chem., **44**, 129 (1903).

² Kolloid-Z., **36**, 129 (1925).

³ J. Phys. Chem., **25**, 742 (1921).

Mukherjee and Chaudhuri² estimated the time required for the same concentration of various salts to make the sol so cloudy that a heated filament a definite distance away was just obscured. From the results obtained they conclude that the influence of anions is negligible except in the case of the so-called complex ions like benzoate, ferricyanide, and salicylate which exert a marked effect. Actually, their data show the precipitating power of iodate and nitrate to be less than that of chloride and bromide. Oxalate has admittedly a lower precipitating power than sulfate

¹ FREUNDLICH: Alexander's "Colloid Chemistry," 593 (1926).

² J. Chem. Soc., **125**, 794 (1924).

which can hardly be attributed to difference in complexity of the ions. It appears, therefore, that Mukherjee's observations support rather than refute the contention that the effect of the anion can not be neglected, even though the procedure probably gives a less accurate measure of precipitating power than carefully determined precipitation values. Following the same general method of procedure, Ostwald¹ demonstrated the effect of

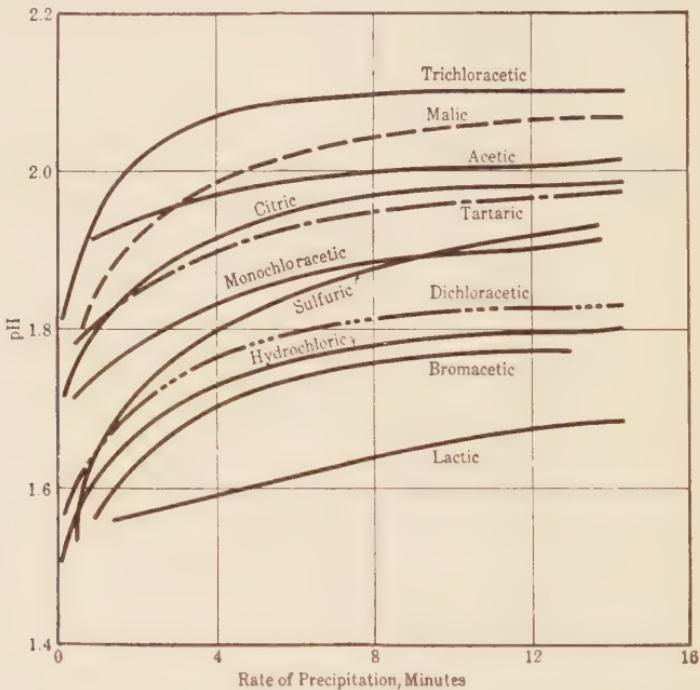


FIG. 2.—Rate of precipitation of arsenic trisulfide sol by acids.

anions by determining the rate of precipitation of arsenic trisulfide sol by various acids. In Fig. 2, the pH of the precipitating electrolytes is plotted against the rate of precipitation. If the hydrogen ion concentration were the only factor, every acid should give the same curve. Since this is not the case, the anion must also be taken into account.

In determining the precipitation values of sols, a uniform procedure as regards stirring should be followed. Thus, if an

¹ *Kolloid-Z.*, **40**, 201 (1926).

arsenic trisulfide sol is shaken continuously, appreciable flocking will result in a given time with a concentration of electrolyte that will cause no flocking whatsoever without stirring.¹ It has been observed repeatedly² that the critical concentration of electrolytes does not cause agglomeration of the neutralized particles into a clump unless the mixture is shaken. What apparently happens is that the charge on the particles is reduced to the critical value but instead of agglomerating into a clump, the individual particles with their film of adsorbed water coalesce to a loose jelly structure that is readily broken up by stirring. If a concentration of electrolyte close to the critical value is used and the sol is allowed to stand quietly for a day or two, the surface of the precipitate as it settles appears to be a fairly strong, translucent, mobile film, strikingly similar in appearance to that of a copper ferrocyanide membrane.

Adsorption during Precipitation of Sol.—Since precipitation takes place when the charge is reduced to a critical value by adsorption of ions of opposite charge, it follows that the necessary reduction in charge should be occasioned by adsorption of equivalent amounts of various ions provided the electrolytes have a common stabilizing ion. In support of this view, Whitney and Ober showed the precipitation of arsenic trisulfide by the chlorides of calcium, strontium, and barium to be accompanied by adsorption of similar amounts of the cations. These observations have been extended by other investigators, as given in Table VIII. On the basis of such data, Freundlich assumes that equivalent amounts of various electrolytes are adsorbed at their precipitation concentration. While the maximum variation from equivalence does not exceed 20 per cent in the above observations, the variation in adsorption of precipitating ions by the hydrous oxides of iron and aluminum is much higher.³ A variation would be expected when we consider that two factors determine the amount adsorbed in a given case, (*a*) adsorption by the electrically charged particles during neutralization, and

¹ FREUNDLICH and BASU: *Z. physik. Chem.*, **115**, 204 (1925); FREUNDLICH and KROCH: *Ibid.*, **124**, 155 (1926); BOUTARIC and VUILLAUME: *Compt. rend.*, **174**, 1351 (1922); cf. Wo. OSTWALD: *Kolloid-Z.*, **41**, 71 (1927).

² WEISER: Colloid Symposium Monograph, **4**, 369 (1926).

³ WEISER: "The Hydrous Oxides," 123 (1926).

TABLE VIII.—ADSORPTION OF CATIONS DURING THE PRECIPITATION OF ARSENIC TRISULFIDE SOL

Metal	Concentration of sol, grams per liter	Adsorption, milliequivalent per gram	Observer
Barium.....	6.4	0.116	Weiser ¹
Strontium.....	6.4	0.107	Weiser
Calcium.....	6.4	0.093	Weiser
Barium.....	11.8	0.060	Weiser
Strontium.....	11.8	0.056	Weiser
Calcium.....	11.8	0.043	Weiser
Barium.....	21.5	0.072	Weiser
Strontium.....	21.5	0.069	Weiser
Calcium.....	21.5	0.073	Weiser
Barium.....	10.0	0.110	Whitney and Ober ²
Strontium.....	10.0	0.082	Whitney and Ober
Calcium.....	10.0	0.100	Whitney and Ober
Aniline.....	0.074	Freundlich ³
New fuchsin.....	0.076	Freundlich
Barium.....	3.33	0.086	Linder and Pieton ⁴
UO ₂	4.14	0.088	Freundlich ⁵
Cerium.....	4.14	0.069	Freundlich

¹ *J. Phys. Chem.*, **29**, 955 (1925).² *J. Am. Chem. Soc.*, **23**, 842 (1901).³ *Kolloid-Z.*, **1**, 321 (1907).⁴ *J. Chem. Soc.*, **67**, 64 (1895).⁵ *Z. physik. Chem.*, **73**, 408 (1910).

(b) adsorption of the neutralized particles during agglomeration. The amounts of (a) will be equivalent but the amounts of (b) will vary with the nature and concentration of the electrolyte. For this reason, Freundlich's assumption that equivalent amounts of various ions are adsorbed at their precipitation value can not be generally true since this would mean either that the neutralized particles do not act as an adsorbent or adsorb all ions to the same extent, both of which are improbable. Moreover, the varia-

bility in the precipitation value will necessarily result in variation in the degree of saturation of the adsorbent by the adsorbed phase. One should expect the adsorption values to approach equivalence more nearly the less the adsorption capacity of the precipitated particles. This doubtless accounts for the values being more nearly equivalent with arsenic trisulfide sol than with hydrous oxides having many times the adsorption capacity. Nevertheless, the author is inclined to believe that the variations with the former are real. Thus, barium seems to be adsorbed a bit more strongly than strontium in every case. The observations with calcium are more erratic, probably because the estimation of very small amounts of this element as oxide are relatively less accurate than the determination of the other alkaline earths as sulfate.

Neglecting the effect of the stabilizing ions of an electrolyte, the precipitating ion which is most readily adsorbed will precipitate in the lowest concentration. From this it follows that the greater precipitating power of ions of higher valence is due to their relatively greater adsorbability.¹ Moreover, among ions of the same valence, the most readily adsorbed will effect precipitation in the lowest concentration. Finally, the variation among electrolytes with the same precipitating ion and different stabilizing ions is due to the difference in the adsorbability of the latter.²

Let us consider an ideal case fulfilling the following requirements:(1) the amounts of precipitating ions adsorbed are equivalent and depend only on the number of charges they carry, and (2) the effect of the stabilizing ion is a logarithmic function of its concentration, that is, follows the usual adsorption isotherm. Now if the amounts adsorbed in mols of the several ions which are proportional to the reciprocal of the valence are plotted against the precipitation concentration in milliequivalents per liter, a curve is obtained as shown in Fig. 3.

As is well known, a much higher equivalent concentration of a univalent ion is required to get the necessary adsorption for neutralization than of a multivalent ion. It is unnecessary, of

¹ P. 288.

² For the effect of solubility and hydration on adsorbability see pp. 187, 217 and 255.

course, to assume, as Freundlich has done, that the equivalent amounts of the ions are adsorbed from equimolar solutions. The isotherm of Fig. 3 is the curve of equivalent adsorption necessary for decreasing the charge to the critical value and must not be confused with the total amount adsorbed on coagulation.

One might expect to approach most nearly the ideal conditions referred to in the preceding paragraph by working with strongly

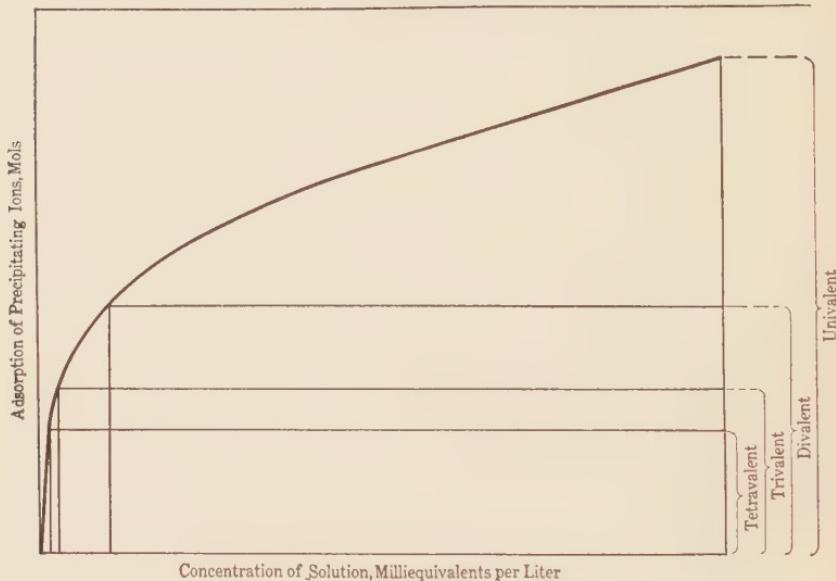


FIG. 3.—Adsorption isotherm for cations of various valences (diagrammatic).

ionized salts having a common stabilizing ion and precipitating ions varying in valence but so similar chemically that the adsorption in mols will be proportional to the reciprocal of the valence. The common stabilizing ion will influence the adsorption of the precipitating ion logarithmically in proportion to the concentration. Such conditions are actually realized approximately in the precipitation of arsenic trisulfide sol by cobalt amines with cations varying in valence from 1 to 6. The precipitation values for a series of such salts as observed by Matsuno,¹ are given in Table IX. In these experiments a relatively small amount of sol was coagulated by an excess of cobalt salt so that the amount adsorbed may be neglected in comparison with the

¹ *J. Coll. Sci., Tokio*, **41**, M 11, 1 (1921); Table IX and Fig. 4.

TABLE IX.—PRECIPITATION VALUES OF COBALT AMINES FOR ARSENIC TRISULFIDE SOL

Salt	Valence of cation	Precipitation values, milliequivalents per liter		
		Ob- served	Aver- age	Calcu- lated
[Co(NH ₃) ₄ C ₂ O ₄]Cl ₂	1	6670		
[Co(NH ₃) ₄ (NO ₂) ₂] ₍₆₎ ⁽¹⁾ [Co(NO ₂) ₆]	1	6000		
[Co(NH ₃) ₄ (NO ₂) ₂] ₍₂₎ Cl ₂	1	5330		
[Co(NH ₃) ₄ CO ₃] ₂ SO ₄	1	5330		
[Co(NH ₃) ₄ (NO ₂) ₂] ₍₂₎ ⁽¹⁾ [Co(NH ₃) ₂] (NO ₂) ₄ Cl ₂	1	5330		
[Co(NH ₃) ₄ (NO ₂) ₂] ₍₆₎ Cl ₂	1	4670		
[Co(NH ₃) ₄ CO ₃]NO ₃ · ½H ₂ O	1	4670	5330	5130
[Co(NH ₃) ₅ NO ₂]Cl ₂	2	800		
[Co(NH ₃) ₅ NO ₂][Co(NH ₃) ₂ (NO ₂) ₄] ₂	2	800		
[Co(NH ₃) ₅ SCN]Cl ₂	2	666		
[Co(NH ₃) ₅ Cl]Cl ₂	2	666		
[Co(NH ₃) ₅ Cl] ₂ (SO ₄ H) ₂ SO ₄	2	666	720	666
[Co en ₃]Cl ₃	3	240		
[Co(NH ₃) ₅ H ₂ O] ₂ (SO ₄) ₃ · 3H ₂ O	3	240		
[Co(NH ₃) ₆]Cl ₃	3	200		
[Co(NH ₃) ₆](NO ₃) ₃	3	200		
[(NH ₃) ₂ Co · (OH) ₃ · Co(NH ₃) ₃]Cl ₃ · H ₂ O	3	160		
[(NH ₃) ₃ Co · (OH) ₃ · Co(NH ₃) ₃](HSO ₄) ₃	3	160	200	200
[(NH ₃) ₅ Co · NH · Co(NH ₃) ₅]Cl ₄	4	83.2		
[(NH ₃) ₄ Co / NH ₂ / Co(NH ₃) ₄]Cl ₄ · 4H ₂ O	4	75.2		
[(NH ₃) ₄ Co · NH ₂ · Co(NH ₃) ₄]Cl ₄ · 4H ₂ O	4	75.2		
[(NH ₃) ₄ Co · (OH) ₂ · Co(NH ₃) ₄]Cl ₄	4	66.8	75.2	88
{CO[HO / HO / CO(NH ₃) ₄] ₃ }Cl ₆	6	25.2	25.8

precipitation value. In other words, the precipitation concentration is essentially the same as the final equilibrium concentration. In Fig. 4 the precipitation values are plotted against the

reciprocal of the valence giving an isotherm similar to the diagrammatic one. In the same figure is plotted also the logarithms of the precipitation values against the logarithms of the reciprocal of the valence. An approximately straight line is obtained from the slope of which one may calculate the precipitation values and compare with the observed values¹ (see Table IX).

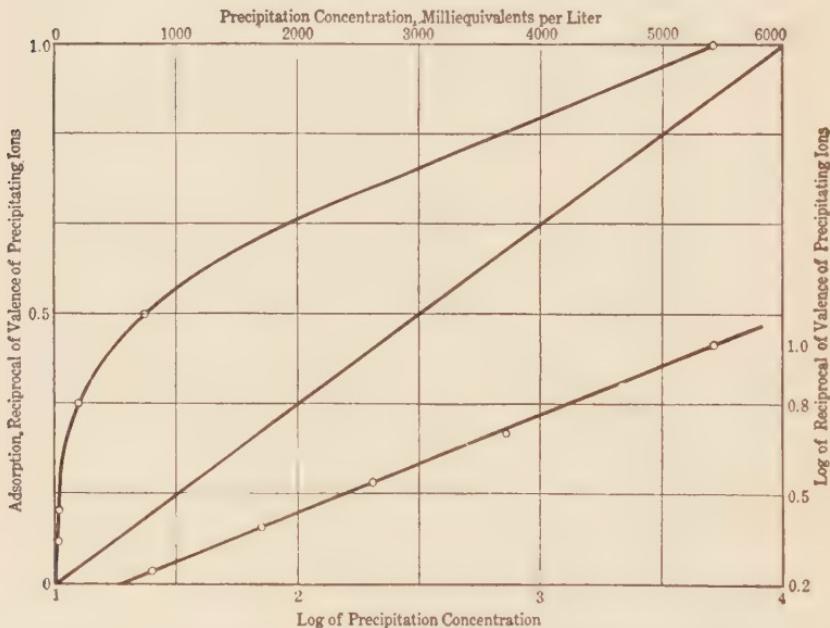


FIG. 4.—Relationship between the valence of cobalt amine cations and the precipitation concentration for arsenic trisulfide sol.

Freundlich and Zeh² confirmed the observations of Matsuno by a study of the effect of the various cobalt amines on the cataphoretic migration velocity of arsenic trisulfide particles. Similar observations on hydrous ferric oxide in the presence of complex cyanide anions of varying valence, revealed a specific adsorption factor in addition to valence. Thus the precipitating power of $\text{Au}(\text{CN})'_4$ appears to be twelve times as great as $\text{Au}(\text{CN})'_2$ and of $\text{Fe}(\text{CN})''_6$, twice as great as $\text{Pt}(\text{CN})''_4$.

¹ Cf. FREUNDLICH: *Kolloid-Z.*, **31**, 243 (1922).

² *Z. physik. Chem.*, **114**, 65 (1924).

Effect of Concentration of Sol.—The precipitation value of arsenic trisulfide sol changes with the concentration as shown by the data recorded in Table X and shown graphically in Fig. 5.¹ The curves were obtained by plotting concentration against ratio of each precipitation value to that of the strongest sol. It will be seen that the precipitation value of potassium chloride increases and of barium and aluminum chloride decreases with dilution of arsenic trisulfide sol, although with many sols the precipitation values of all electrolytes fall off as the sol is diluted.² Kruyt and van der Spek³ recognize the existence of two factors which determine change in precipitation value with dilution of sol: first, the smaller number of particles which will require the

TABLE X.—PRECIPITATION OF ARSENIC TRISULFIDE SOLS

Concentration of sol, per cent	Precipitation values in milliequivalents per liter of		
	KCl	BaCl ₂	AlCl ₃
100 (6.24 grams per liter)	68.3	1.940	0.513
75	68.3	1.877	0.473
50	70.0	1.800	0.380
25	76.7	1.733	0.333
10	80.0	1.683	0.260

adsorption of *less* precipitating ion to lower the charge to the critical value; and second, the greater distance between the particles, which makes collision less probable, and so necessitates a greater reduction in particle charge by the adsorption of *more* of the precipitating ion. Since these two factors have opposite effects, it is only necessary to assume the predominating influence of one or the other to account for the results in a given case. Thus, for arsenic trisulfide Kruyt assumes the important factor to be the lessened chance of collision with

¹ WEISER and NICHOLAS: *J. Phys. Chem.*, **25**, 742 (1921); KRUYT and VAN DER SPEK: *Kolloid-Z.*, **25**, 1 (1919); BURTON and BISHOP: *J. Phys. Chem.*, **24**, 701 (1920); BURTON and MACINNES: *Ibid.* **25**, 517 (1921).

² Cf. WEISER: "The Hydrous Oxides," 57 (1926).

³ *Kolloid-Z.*, **25**, 1 (1919).

potassium ion, and a decrease in the required amount to be adsorbed with barium and aluminum ions. If the decreased chance of collision were the only factor in preventing a weaker sol from coagulating in a given time in the presence of enough potassium chloride to coagulate a stronger sol, it would seem that complete coagulation of the weaker sol should result if sufficient time were allowed. As a matter of fact, however, enough potassium chloride to precipitate in 2 hours a sol containing

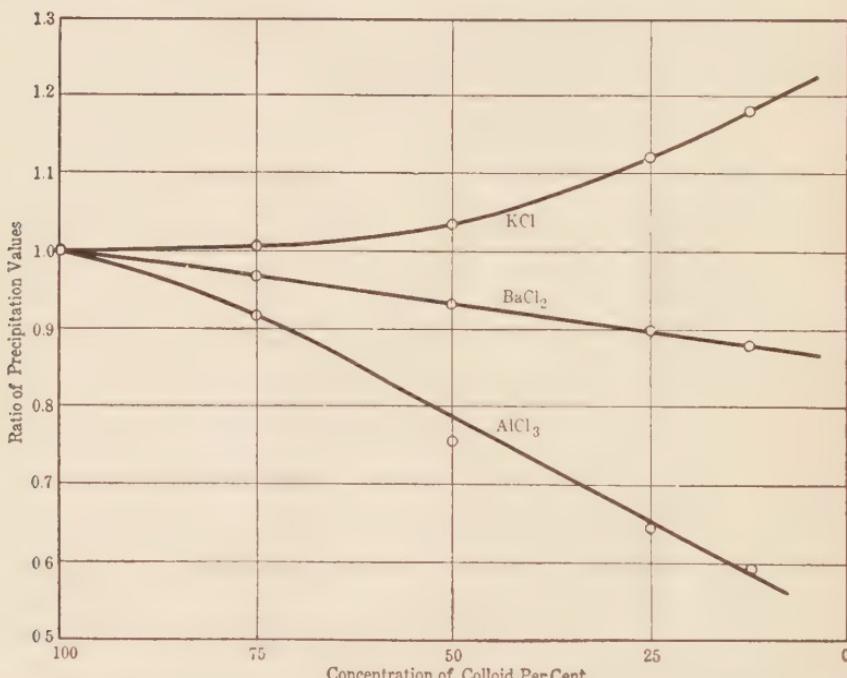


FIG. 5.—Effect of concentration of arsenic trisulfide sol on the stability toward electrolytes.

5 grams per liter will not precipitate a sol one-fourth as strong in several weeks. Other observations indicate that Kruyt attaches too much importance to the decreased chance of collision of particles on dilution of sol. Thus, the precipitation value varies almost directly with the concentration of sol for precipitating ions of high valence.

That Kruyt's hypothesis should not be entirely adequate might be expected since he was concerned only with the precipitating

ions of electrolytes, disregarding entirely the effect of adsorption of the stabilizing ions having the same charge as the sol. If the adsorption of the stabilizing ion is negligible and the adsorption of the precipitating ion is very large, there will be a tendency for the precipitation value to vary directly with the concentration of sol. This condition is realized experimentally with electrolytes having multivalent precipitating ions. As would be expected, the greater the valence of the precipitating ion and hence the lower the precipitation value, the more nearly we find the latter varying directly with the concentration of the sol. If the adsorption of the stabilizing ion of an electrolyte is appreciable, the precipitation value is increased. This effect will be more pronounced the greater the dilution of sol, since the decreased chance both of collision and of coalescence will combine to make the sol proportionally more stable so that correspondingly more of the precipitating ion must be added for complete precipitation. The influence of the stabilizing ion is more marked with electrolytes having univalent precipitating ions which precipitate only in relatively high concentrations. Under these conditions, the precipitation value decreases with dilution much less than with multivalent precipitating ions and may even increase as the sol is diluted.

It is frequently noted that less electrolyte is required for precipitation of a sol when added all at once than when added stepwise through a long interval of time. This phenomenon is known as "acclimatization," the connotation being that the colloid becomes acclimatized to its surroundings when the electrolyte is added slowly and so more is required to produce a given result. It would appear, however, that the necessity for using more electrolyte to effect complete precipitation on slow addition arises not so much from the adaptability of the sol to the presence of electrolytes as from fractional precipitation which not only removes ions owing to adsorption by neutralized particles but alters the stability of the sol by decreasing its concentration. From this point of view, the factors which determine the excess required for a given slow rate of addition are: the extent to which the colloid undergoes fractional precipitation, the adsorbing power of the precipitated colloid, the adsorption of the precipitating ions, and the effect of dilution of sol on the pre-

cipitation concentration. Bancroft¹ adds that slow agglomeration probably decreases the adsorbing power of the colloid, a view that is in line with what we know of anomalous adsorption and the ageing of precipitates.

Action of Non-electrolytes.—The addition of non-electrolytes to sols usually decreases their stability. Thus, Billitzer² found that a negatively charged platinum sol can be sensitized, discharged, or even made positive by the addition of suitable amounts of alcohol. Klein³ showed that negative charged sols of arsenic trisulfide, gold, silica, and ferric oxide are agglomerated in part by alcohols, whereas positive sols are not. More striking results are obtained in the presence of electrolytes. Although non-electrolytes appear to have a more pronounced destabilizing action on negatively charged sols, it is by no means confined to them. Thus Freundlich and Rona⁴ observed that the addition of camphor, thymol, and urethanes to ferric oxide sol reduces the precipitation concentration of sodium chloride and the same is true for the action of phenol and isoamyl alcohol on the sols of chromic oxide and ferric oxide.⁵ Moreover, Kruyt and van der Made⁶ precipitated hydrous ceric oxide as a jelly by the addition of alcohol.

The sensitization of sols by non-electrolytes has been attributed by Wolfgang Ostwald⁷ and Cassuto⁸ to a decrease in the dielectric constant of the medium. In line with this, Keeser⁹ finds arsenic trisulfide sol to be stabilized by the addition of urea or glycocoll, both of which increase the dielectric constant of water.¹⁰ Freundlich¹¹ suggests that the sensitization results from the lowering of the charge on the particles by adsorption on their surface of

¹ "Applied Colloid Chemistry," 297 (1926).

² *Z. physik. Chem.*, **45**, 312 (1903).

³ *Kolloid-Z.*, **29**, 247 (1921).

⁴ *Biochem. Z.*, **81**, 87 (1917).

⁵ WEISER: *J. Phys. Chem.*, **28**, 1253 (1924).

⁶ *Rec. trav. chim.*, **42**, 294 (1923).

⁷ "Grundriss der Kolloidchemie," 441 (1909).

⁸ "Der Kolloide Zustand der Materie," 152 (1913).

⁹ *Biochem. Z.*, **157**, 166 (1925); cf., however, GHOSH and DHAR: *J. Phys. Chem.*, **29**, 668 (1925).

¹⁰ FÜRTH: *Ann. Physik*, **70**, 63 (1923).

¹¹ "Kapillarchemie," 637 (1922).

the organic non-conductor, which has a dielectric constant appreciably lower than that of water. Thus, the charge e on a particle is

$$e = \frac{\xi Dr(r + d)}{d}$$

where ξ is the potential difference of the double layer at the surface of a spherical particle of radius r , D the dielectric constant, and d the thickness of the double layer. From this it follows that a decrease in D will lower e and, hence, the precipitation value.

The dielectric constant of the non-electrolyte is not the only factor which influences the stability since sugar apparently acts as a stabilizer for sols¹ and one is not justified in ascribing the difference between alcohol and sugar to the dielectric constant. That sugars are adsorbed by sulfide sols is evidenced by a loss in rotatory power when they are dissolved in the sols instead of in water.² In certain cases, the variation in adsorption with the concentration of sugar can be formulated quite accurately by the Freundlich equation.³

Kruyt and van Duin⁴ found the effect of non-electrolytes on the precipitation value of electrolytes for arsenic trisulfide sol to be determined by the nature of the precipitating ion; with univalent and trivalent ions, it was lowered, while with bivalent ions it was raised. For any given electrolyte, the change in precipitation value was independent of the dielectric constant of the non-electrolyte employed.

From a study of this behavior in the author's⁵ laboratory the sensitizing action of non-electrolytes was attributed, at least in part, to the displacing of a stabilizing ion or the cutting down of the adsorption of a precipitating ion. These two actions are antagonistic and so the precipitation value may be increased, decreased, or remain unchanged in the presence of a non-electrolyte. Some data bearing on this question are recorded in Table

¹ GHOSH and DHAR: *J. Phys. Chem.*, **29**, 668 (1925).

² BHATNAGAR and SHRIVASTAVA: *J. Phys. Chem.*, **28**, 730 (1924).

³ PRASAD, SHRIVASTAVA, and GUPTA: *Kolloid-Z.*, **37**, 101 (1925).

⁴ *Kolloidchem. Beihefte*, **5**, 270 (1914); cf., also, BOUTARIC and SEMELET: *Rev. gén. Colloides*, **4**, 268 (1926).

⁵ WEISER: *J. Phys. Chem.*, **28**, 1254 (1924); cf., also, JANEK and JIRGENSONS: *Kolloid-Z.*, **41**, 40 (1927).

XI and shown graphically in Fig. 6. An arsenic trisulfide sol was coagulated with the precipitation concentration of barium chloride with and without non-electrolyte and the adsorption of barium determined. Comparing the results of experiments I and II, it will be seen that the adsorption is less in the presence of phenol although the amount of electrolyte necessary to effect precipitation is greater. This means that the sol is sensitized in the sense that less barium ion must be adsorbed in order to lower the charge on the particles below the critical value. The fact that a higher concentration of barium must be present to

TABLE XI.—ADSORPTION OF BARIUM BY ARSENIC TRISULFIDE SOL IN THE PRESENCE OF NON-ELECTROLYTE

Experiment number	Solutions mixed with 100 cubic centimeters of sol containing 31.5 grams As_2S_3				Barium adsorbed, grams per mol As_2S_3
	$N/50$ BaCl_2 , cubic centimeters	Phenol, cubic centimeters	$N/100$ AlCl_3 , cubic centimeters	H_2O , cubic centimeters	
I	31.40	0	0.0	68.6	0.805
II	42.35	50	0.0	7.65	0.708
III	31.40	50	3.6	15.00	0.657
IV	20.00	50	8.3	21.70	0.538
V	10.00	50	11.8	28.20	0.381
Isoamyl alcohol					
VI	39.36	50	0.0	10.64	0.753
VII	31.40	50	2.5	16.10	0.713

cause precipitation of the sensitized sol, is due to the marked cutting down of the adsorption of barium ion by the phenol.

Whereas the cutting down of adsorption of the precipitating ion predominates over the increase in sensitivity with barium chloride, this is not the case with potassium chloride, which shows a lower precipitation value in the presence of phenol. This is probably due to the relatively flat character of the adsorption isotherm for univalent precipitating ions. With such ions, the change in adsorption is usually very slight for relatively large changes in concentration; conversely, a slight decrease in

the adsorption necessary for lowering the charge below the critical value is marked by such a decided lowering of the precipitation value that this effect predominates over the decreased adsorption of the precipitating ion.

Contrary to Kruyt and van Duin's observations, the precipitation value of aluminum salts is not changed appreciably by

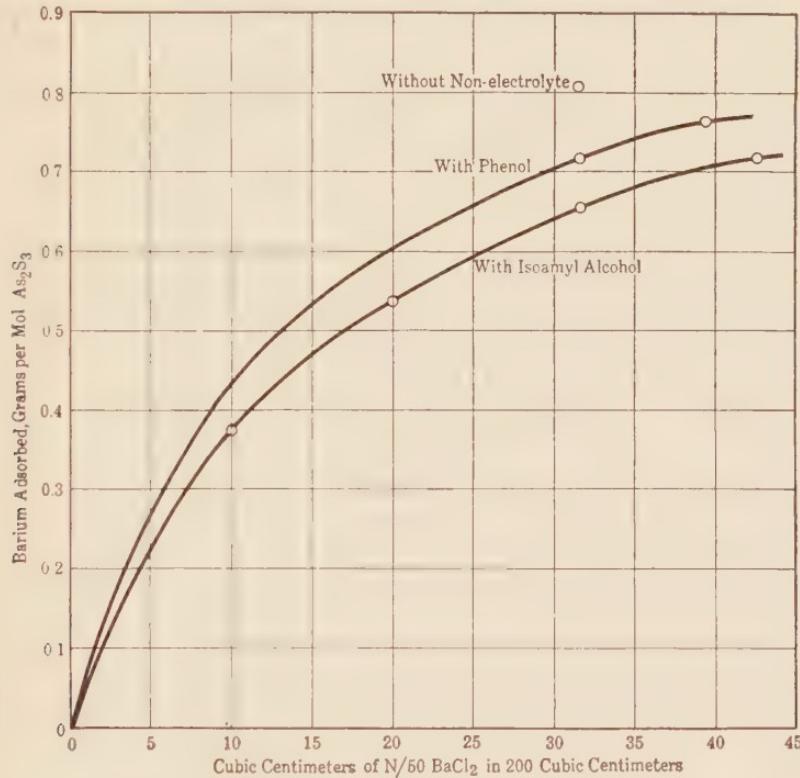


FIG. 6.—Adsorption of barium ion by arsenic trisulfide in the presence of non-electrolytes.

the presence of non-electrolytes. The precipitation value of potassium sulfate and potassium oxalate for the sols of hydrous ferric and chromic oxide is changed but little by the presence of phenol and isoamyl alcohol; and the adsorption of these ions by the precipitated oxides is approximately the same with and without the non-electrolytes.

If ether is added to an arsenic trisulfide sol followed by the addition of alcohol to form two liquid layers, there is a distribu-

tion of the sulfide between the two layers, in amounts depending on the conditions.¹ Corliss² in Lash Miller's laboratory investigated quantitatively the distribution throughout the system water-ether-alcohol and found that the ratio of distribution in the two layers varies continuously with the composition of the phases; and that, other things being equal, the fraction of the arsenic trisulfide going into the upper (more ethereal) layer decreases with increasing concentration of sulfide. Reinders³ reports that colloidal arsenic trisulfide stays in the water when shaken with carbon tetrachloride, benzene, or ether; but precipitates out at the dimeric interface between the two layers when shaken with amyl alcohol or butyl alcohol. The theory of this action will be considered in Chap. IX.

Corliss claims that sols containing alcohol and ether are more stable toward electrolytes than pure aqueous sols but this is not justified by his experimental data. Sen⁴ finds that sucrose and ethyl alcohol stabilize a manganese dioxide sol toward copper sulfate and silver nitrate, and sucrose sensitizes it slightly toward silver nitrate. To explain this anomalous behavior, the effect of the non-electrolyte on the hydrogen ion concentration and the viscosity must be taken into account. The increase in adsorption of copper sulfate by air-dried manganese dioxide in the presence of alcohol, gives no definite indication of the effect of alcohol on the adsorption of copper ion by manganese dioxide sol at constant hydrogen ion concentration.

Mutual Action of Sols.—Mutual precipitation takes place on the addition of suitable amounts of positive and negative sols. The order of precipitating power of a number of positive sols for negative arsenic trisulfide sol is:⁵ $\text{Fe}_2\text{O}_3 < \text{ThO}_2 < \text{CeO}_2 < \text{ZrO}_2, \text{Al}_2\text{O}_3 < \text{Cr}_2\text{O}_3$. For antimony trisulfide sols the order is the same except that alumina is more effective than chromic oxide in precipitating antimony trisulfide and much less effective in precipitating arsenic trisulfide. Moreover, ZrO_2 is just as

¹ MILLER and MCPHERSON: *J. Phys. Chem.*, **12**, 706 (1908); ZSIGMONDY: *Kolloid-Z.*, **13**, 105 (1913).

² *J. Phys. Chem.*, **18**, 681 (1914).

³ *Kolloid-Z.*, **13**, 235 (1913); cf. VON WEIMARN and ALEXEJEW: *J. Russ. Phys. Chem. Soc.*, **46**, 133 (1914); JANEK: *Chem. Zentr.*, I, 1160 (1924).

⁴ *Kolloid-Z.*, **38**, 310 (1926).

⁵ BILTZ: *Ber.*, **37**, 1095 (1904).

effective as Al_2O_3 on As_2S_3 sol whereas it is much less effective than either Al_2O_3 or Cr_2O_3 on Sb_2S_3 sol. Since neutralization with mutual precipitation takes place when one sol has adsorbed the amount of the sol carrying an equivalent amount of ion having the opposite charge, it follows that the amount of one sol required to precipitate a given amount of another sol will vary with the adsorbability. The action will, therefore, be specific¹ and not additive as is usually assumed.²

In certain cases precipitation takes place when sols of the same charge are mixed. Thus, mixtures of the negative sols of arsenic trisulfide and sulfur are unstable in the presence of each other owing to interaction between the respective stabilizing electrolytes, hydrogen sulfide, and a thionic acid.³ This observation suggested to Thomas and Johnson⁴ that the mutual precipitation of oppositely charged sols is due to interaction between the stabilizing electrolytes. This cannot be generally true since mutual precipitation takes place very frequently where interaction between stabilizing agents is a remote possibility.

Mixtures of arsenic trisulfide sol and silver sol interact on standing, giving distinct color changes.⁵ In darkness, the color goes from greenish brown to a cognac or lilac color. In the light, the color passes through a series of green and blue tones into a golden yellow. In the dark there is apparently a mutual adsorption of particles of like charge giving mixed particles of a lilac color. This change is prevented by the addition of gelatin which keeps the particles separated.⁶ In the light, a chemical change takes place with the formation of a silver salt, possibly silver thioarsenite.⁷ Börjeson⁸ plated gold on colloidal sulfide particles by reducing gold chloride with hydrogen peroxide in the presence of the particles which acted as nuclei.

¹ BANCROFT: "Applied Colloid Chemistry," 307 (1926).

² FREUNDLICH: "Kapillarchemie," 445 (1909); THOMAS: Bogue's "Colloidal Behavior," 1, 325 (1924).

³ FREUNDLICH and NATHANSON: *Kolloid-Z.*, 28, 258; 29, 16 (1921).

⁴ *J. Am. Chem. Soc.*, 45, 2532 (1923).

⁵ FREUNDLICH and MOOR: *Kolloid-Z.*, 36, 17 (1925); BHATNAGAR, YAJNIK, and ZADOO: *Quart. J. Indian Chem. Soc.*, 4, 209 (1927).

⁶ Cf. PESKOV: *Kolloid-Z.*, 32, 24 (1923).

⁷ PAULI and SEMLER: *Kolloid-Z.*, 34, 145 (1924).

⁸ *Kolloid-Z.*, 27, 18 (1920).

Although gelatin is usually regarded as a protective colloid for sols, cutting down the precipitating action of electrolytes, Billitzer¹ showed that sols of the sulfides of arsenic and antimony are precipitated by small amounts of gelatin. In larger amounts it adsorbs the arsenic trisulfide converting the whole into a stable positive sol. The sensitization of arsenic trisulfide sols toward electrolytes by the addition of small amounts of gelatin has been observed repeatedly.² Peskov³ claims, however, that highly purified gelatin sols are unable to cause coagulation of other sols unless the former are concentrated and contain large particles. Negatively charged gelatin in small concentrations may precipitate negative arsenic trisulfide sol probably by adsorbing the peptizing ion and thus reducing the charge.⁴ Müller and Artmann⁵ report that gum and casein are better protective colloids for arsenic trisulfide sol than are glue and isinglass. Sodium and potassium soaps protect the sol in the following order: Linoleate > oleate > palmitate > stearate > myristate > laurate.⁶

Keeser⁷ found that salts of cholesterol and lecithin sensitize arsenic trisulfide sols toward electrolytes. The activity of the sols of cholesterol esters in cutting down the stability of negative sols is reduced as the length of the carbon chain in the homologous series is decreased. The sensitizing action of the potassium and sodium salts of cholesterol sulfuric acid depends on the solubility of the salt. The constant ratio in the organism between free cholesterol and its esters may have an important bearing on the physical state of the body colloids. If poisons are removed from the body by combining with free cholesterol, such as happens in the removal of saponin, the normal physical condition of the cell colloids could be disturbed in case the

¹ *Z. physik. Chem.*, **51**, 145 (1905).

² BOUTARIC and PERREAU: *Compt. rend.*, **181**, 511 (1925); SUGDEN and WILLIAMS: *J. Chem. Soc.*, **129**, 2424 (1926); GHOSH and DHAR: *Kolloid-Z.*, **41**, 229 (1927).

³ *J. Russ. Phys. Chem. Soc.*, **49**, 1 (1917).

⁴ PESKOV and SOKOLOV: *J. Russ. Phys. Chem. Soc.*, **58**, 823 (1926).

⁵ *Chem. Zentr.*, I, 1388 (1904).

⁶ PAPACONSTANTINOU: *J. Phys. Chem.*, **29**, 319 (1925); cf. BHATNAGAR, PRASAD, and BAHL: *Quart. J. Indian Chem. Soc.*, **2**, 11 (1925).

⁷ *Biochem. Z.*, **154**, 321 (1924); **157**, 166 (1925).

resulting product has the properties of a cholesterol ester. This point of view may serve to account for the fact that an increase in the amount of cholesterol in the organism is always followed by an increase in the fatty acid phosphatides.

ARSENIC TRISULFIDE ORGANOSOLS

Bikerman¹ prepared stable organosols of arsenic trisulfide in

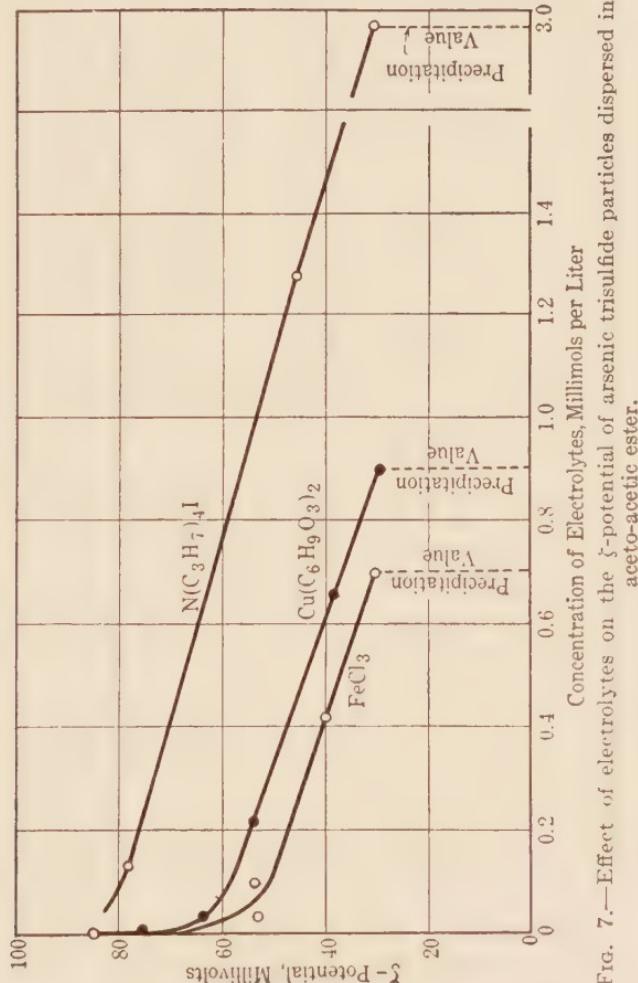


FIG. 7.—Effect of electrolytes on the ζ -potential of arsenic trisulfide particles dispersed in aceto-acetic ester.

nitrobenzene and acetoacetic ester by dissolving arsenic trichloride in the respective solvents, conducting dry hydrogen sulfide

¹ *Z. physik. Chem.*, **115**, 261 (1925).

through the solutions, and finally washing out the excess hydrogen sulfide and hydrogen chloride with a current of air. The sols are charged negatively, the ξ -potential of the particles being similar to that in water. Bikerman measured the variation in ξ -potential in the usual way on adding increasing amounts of electrolytes containing cations of varying valence. The data are rather unsatisfactory, probably because different sols were used for each salt so that the results are not strictly comparable. The results of some observations on the acetoacetic ester sol are given in Table XII and shown graphically in Fig. 7. It will be seen that the decrease in the ξ -potential of the particles

TABLE XII.—EFFECT OF ELECTROLYTES ON THE ξ -POTENTIAL OF ARSENIC TRISULFIDE PARTICLES

Electrolyte	Concentration C , millimols per liter	ξ -potential millivolts
FeCl_3	0.00123	85
	0.0036	80
	0.038	52
	0.110	53
	0.422	40
$\text{Cu}(\text{C}_6\text{H}_9\text{O}_3)_2$	0.0011	78
	0.0113	65
	0.220	53
	0.660	38
$\text{N}(\text{C}_3\text{H}_7)_4\text{I}$	0.134	78
	1.280	46

for a given molar concentration is $\text{FeCl}_3 > \text{Cu}(\text{C}_6\text{H}_9\text{O}_3)_2 > \text{N}(\text{C}_3\text{H}_7)_4\text{I}$. The precipitation value for FeCl_3 is 0.7 millimol per liter and for $\text{Cu}(\text{C}_6\text{H}_9\text{O}_3)_2$ is 0.9 millimol per liter while the value for $\text{N}(\text{C}_3\text{H}_7)_4\text{I}$ is about 4.0 millimols per liter. If all the values are given in equivalents, the curve for the iron salt will be above that for the copper salt at the higher concentrations and the precipitation value for the former will be below that of the latter, as it should be. The critical coagulation potential is in the neighborhood of 30 millivolts.

The experiments with the nitrobenzene sol show that the valency rule holds qualitatively provided highly ionized salts are used, although the difference in the precipitating power of ions of varying valence is much less marked than in aqueous sols. Thus to reduce the ξ -potential to 50 millivolts requires 1.26 milliequivalents per liter of $N(C_3H_7)_4I$ and 0.75 milliequivalent per liter of $FeCl_3$. For a sol containing 12 grams arsenic trisulfide per liter the precipitation value of ferric chloride is 1.1 milliequivalents per liter; and for a sol containing 1.5 grams arsenic trisulfide per liter the precipitation value of $Cu(C_6H_9O_3)_2$ is 20 milliequivalents per liter. $N(C_3H_7)_4I$ is not soluble enough to precipitate the sol. The large difference between the iron and copper salt is probably due to the relatively low ionization of $Cu(C_6H_9O_3)_2$ in nitrobenzene.

It is of interest that the charge on arsenic trisulfide organosols can be reversed like the aqueous sols by adding an excess of a salt with a strongly adsorbed cation. Thus a nitrobenzene sol containing 0.6 gram arsenic trisulfide per liter is precipitated by 0.33 milliequivalent per liter of ferric chloride; but 8.4 milliequivalents of ferric chloride per liter gives it a charge of +55 millivolts.

CHAPTER III

COLLOIDAL SULFIDES OF ANTIMONY, BISMUTH, TIN, AND LEAD

COLLOIDAL ANTIMONY TRISULFIDE

Antimony trisulfide occurs in nature as black rhombic crystals known as stibnite. The alchemist "Basil Valentine"¹ prepared an amorphous red sulfide by subliming stibnite with ammonium chloride. In this way, antimony trichloride and ammonium sulfide were first formed and reacted on cooling to give the original compounds, the trisulfide separating as a red powder. Glauber and also Lenery speak of the solution of stibnite in caustic alkalies and the subsequent precipitation of a red powder but it was not until 1714 that particular attention was called to the preparation. In that year Simon, a Carthusian monk, was reported to have restored another monk to health by the administration of the powder prepared by a German apothecary, a disciple of Glauber. Simon gave to the powder the name *alkermes* or *kermes* mineral by which it is still known. The original method of formation consisted in boiling the crude sulfide with alkali until a clear solution was obtained from which the kermes separated. The body was at first believed to be a compound of antimony, sulfur, and alkali but it is now known to be antimony trisulfide with more or less antimony trioxide and adsorbed alkali. The presence of impurities was objectionable for its use as a therapeutic agent so that in later modifications of the original process, the solution and subsequent precipitation of the sulfide were carried out in the absence of air and any trioxide was extracted with tartaric acid.

By passing hydrogen sulfide into a slightly acidified antimonous salt solution, the trisulfide is thrown down as a hydrous mass varying in color from golden yellow to orange red, depending

¹ Cf. ROSCOE and SCHORLEMMER: "Treatise on Chemistry," 2, 1019 (1923).

on the conditions of precipitation. When obtained from chloride solution it adsorbs chloride¹ and the precipitate dried at 105° usually contains a small amount of sulfur, probably from the oxidation of adsorbed hydrogen sulfide. The precipitated compound adsorbs water quite strongly. Prolonged drying over sulfuric acid is reported to give a dihydrate, $Sb_2S_3 \cdot 2H_2O$,² but this composition is doubtless an accidental result of the conditions of drying. When dried at 100° it still retains adsorbed water which is given up gradually on heating to higher temperatures.³ In order to remove all the water in the quantitative estimation of antimony as trisulfide,⁴ it is necessary to heat the amorphous precipitate in a current of carbon dioxide until it goes over to the black crystalline form which adsorbs very little water.

If a dilute hydrochloric acid solution of antimony trichloride is treated with a solution of sodium thiosulfate, a bright red sulfide is obtained which is known as crimson sulfide, antimony cinnabar, and antimony vermillion. The color and composition depends on the method of formation but it always consists of antimony trisulfide with more or less sulfur. X-ray examination⁵ of the various precipitated sulfides show them to be without a definite crystalline structure. If heated to a temperature around 200° they are converted into black crystalline Sb_2S_3 having the same crystal structure as the mineral stibnite. The effect of method of preparation on the physical character and color and the factors influencing the transformation to the crystalline modification will be considered in detail in the chapter on the sulfide pigments (pp. 112 to 115).

Antimony trisulfide, like the corresponding arsenic compound, is hydrolyzed by boiling water.⁶ In the presence of 9 normal hydrochloric acid the orange sulfide goes over to the black crystalline compound quite rapidly at the boiling point.⁷ This

¹ YOUTZ: *J. Am. Chem. Soc.*, **30**, 975 (1908).

² DITTE: *Compt. rend.*, **102**, 212 (1886).

³ DE BACHO: *Ann. chim. applicata*, **12**, 143 (1919); *Chem. Abstr.*, **14**, 1497 (1920).

⁴ FRESENIUS-COHN: "Quantitative Chemical Analysis," **1**, 397 (1908).

⁵ CURRIE: *J. Phys. Chem.*, **30**, 236 (1926).

⁶ ELBERS: *Chem. Ztg.*, **12**, 355 (1888).

⁷ MITCHELL: *Chem. News*, **67**, 291 (1893).

process goes on slowly even at ordinary temperatures. Thus, 2 grams of the orange trisulfide in 5 cubic centimeters of 12 normal, 7 normal, and normal hydrochloric acid are transformed completely into the black crystals in 0.5 day, 1 day, and 10.5 days, respectively. Phosphoric, acetic, and sulfuric acids have little or no influence on the transformation within 2 months.¹

Stibnite is an important constituent of many military and sporting arms primers. For this purpose it need not be pure.² The crystalline trisulfide is also employed in the manufacture of safety matches. The match is tipped with a mixture of the sulfide, potassium chlorate, and powdered glass which is not sufficiently sensitive to be ignited by ordinary friction but inflames promptly when rubbed upon the mixtures of red phosphorus and glass coating the side of the box.

ANTIMONY TRISULFIDE SOLS

A very dilute yellow antimony trisulfide sol is obtained by passing hydrogen sulfide into a saturated solution of antimony trioxide in water. More concentrated sols can be obtained by conducting hydrogen sulfide into a solution of potassium antimony tartrate or of the oxide dissolved in tartaric acid.³ The maximum concentration of antimony salt that can be employed will give a sol containing approximately 5 grams of trisulfide per liter. If higher salt concentrations are used the sulfide is precipitated as a gel. The most satisfactory method of preparing the sol⁴ consists in allowing 200 cubic centimeters of a tartar emetic solution to drop slowly into a like volume of water saturated with hydrogen sulfide through which the gas is kept bubbling. The excess hydrogen sulfide may be removed by a current of hydrogen or by boiling, although the latter procedure is not recommended as the size of the particles is increased and the stability of the sol is reduced. The sols may be purified to a certain extent by dialysis, but if the process is continued too long all the sulfide separates out. To increase the stability of the sols

¹ WILSON and McCROSKEY: *J. Am. Chem. Soc.*, **43**, 2178 (1921); cf. LANG: *Ber.*, **18**, 2716 (1885); DITTE: *Compt. rend.*, **102**, 212 (1886).

² CUSHMAN: *Ind. Eng. Chem.*, **10**, 376 (1918).

³ SCHULZE: *J. prakt. Chem.*, [2] **27**, 320 (1883); cf. HEYER: Crell's "Chem. Ann." **2**, 227, 321, 493 (1785).

⁴ BILTZ: *Ber.*, **37**, 1097 (1904).

so they can be sterilized for therapeutic purposes, Wolvekamp¹ uses the sodium salts of protalbinic and lysalbanic acids as protective colloids. Soap² is also adsorbed by antimony trisulfide and acts as a protective colloid. Utzino³ ground antimony trisulfide in a colloid mill with grape sugar, obtaining sols which appear to show a maximum stability not at the finest state of subdivision. Other conditions being the same, this result cannot be correct. The adsorption of such sugars as arabinose, maltose, and levulose at varying concentrations by antimony trisulfide sol has been followed⁴ by means of the polarimeter, since adsorbed sugar does not affect the plane of polarized light. In certain cases the increase in adsorption with increasing concentration of sugar can be represented quite accurately by the Freundlich equation.

The color of antimony trisulfide sols varies widely with the dilution, as indicated in Table XIII. Like the corresponding

TABLE XIII.—INFLUENCE OF CONCENTRATION ON THE COLOR OF Sb_2S_3 SOLS

Ratio		Color
	$\text{Sb}_2\text{S}_3 : \text{H}_2\text{O}$	
1	200	Deep red; clear in transmitted light, cloudy brown red by reflected light
1	400	Raspberry red
1	600	Deep yellow red
1	1,000	Reddish yellow to yellow
1	10,000	Yellow like dilute ferric chloride
1	100,000	Very light wine yellow
1	1,000,000	Faint yellow in layers at least 15 centimeters thick

arsenic sol, it makes a difference whether a dilute sol is prepared directly or whether a concentrated sol is diluted, in that the latter always contains larger particles and so appears more cloudy in reflected light.⁵ The absorption spectrum of the sol is a continuous band from the violet to the blue.⁶

¹ U. S. Patent, 1412438 (1922).

² BHATNAGAR, PRASAD, and BAHL: *Quart. J. Indian Chem. Soc.*, **2**, 11 (1925).

³ *Kolloid-Z.*, **32**, 149 (1923).

⁴ PRASAD, SHRIVASTAVA, and GUPTA: *Kolloid-Z.*, **37**, 101 (1925).

⁵ BILTZ and GEIBEL: *Nachr. königl. Ges. Wiss. Göttingen*, 141 (1906).

⁶ LINDER and PICTON: *J. Chem. Soc.*, **61**, 133 (1892).

Antimony trisulfide sol is negatively charged owing to adsorption of hydrosulfide and tartrate ions. When not dialyzed, it is more stable toward electrolytes than the corresponding arsenic trisulfide sol but the stability can be varied through wide limits by varying the duration of the dialysis. On account of the similarity between the two sols, one might expect the order of electrolytes arranged according to their precipitating power to be approximately the same for both, as the experiments show.¹ Moreover, the effect of concentration of sol on the precipitation values of electrolytes containing cations of varying valence is similar to that for arsenic trisulfide sol.² The stability of antimony trisulfide sol decreases with age and there is always more or less precipitation of the sulfide together with sulfur after standing for a long time. It is probable that the sol undergoes a photochemical decomposition similar to that observed with arsenic trisulfide sol.³

Jableczynski⁴ followed the velocity of coagulation of antimony trisulfide sol with potassium chloride using a spectrophotometer, and found the process to take place in accord with Smoluchowski's equation,⁵ both in the presence and the absence of an excess of hydrogen sulfide. It will be recalled that the coagulation of an arsenic trisulfide sol does not proceed in accord with Smoluchowski's theory when the sol is freed from hydrogen sulfide. This difference in behavior of the two sols calls for further investigation, as does the accuracy of the experimental method employed by Jableczynski.

COLLOIDAL ANTIMONY PENTASULFIDE AND TETRASULFIDE

A century ago Berzelius⁶ reported that antimony pentasulfide is formed by the action of hydrogen sulfide on a solution of antimonic acid. Bunsen⁷ showed this to be true, provided the

¹ SCHILOW and ORLOWA: *Z. physik. Chem.*, **100**, 425 (1922); *Kolloidchem. Beihefte*, **18**, 1 (1923).

² GHOSH and DHAR: *Kolloid-Z.*, **36**, 129 (1925)

³ See p. 25.

⁴ JABLCZYNSKI and PRZEJDZIECKA-JADRZEJOWSKA: *Bull. soc. chim.*, **37**, 608 (1925).

⁵ See p. 29.

⁶ *Pogg. Ann.*, **7**, 2 (1826); cf., however, ROSE: *Ibid.*, **107**, 186 (1859).

⁷ *Liebig's Ann.*, **192**, 305 (1878).

precipitation is effected by adding rapidly an excess of a saturated solution of hydrogen sulfide to the acid. This procedure was recommended by Bunsen for the quantitative estimation of antimony and for the separation of antimony and arsenic. Bunsen's observations were not confirmed by Wilm,¹ Mourlot,² and Thiele,³ who found the precipitated sulfide to contain sulfur easily extractable with a sulfur solvent. Brauner⁴ and later Bôsek⁵ did much toward clearing up the matter by showing that pure pentasulfide is formed only in case Bunsen's directions are followed exactly. To get the compound pure, care must be taken to get all the antimony in the pentavalent state and to add the hydrogen sulfide solution rapidly in the cold to the antimonious solution containing 10 to 20 per cent of hydrochloric acid. If the precipitation is accomplished by conducting hydrogen sulfide slowly into a solution containing but little hydrochloric acid, a part of the pentavalent antimony is reduced and the resulting precipitate is a mixture of pentasulfide, trisulfide, and sulfur.⁶ In general, the reduction was found to be greater the slower the stream of hydrogen sulfide and the higher the temperature.

Pure antimony pentasulfide prepared by Bunsen's method is a rich orange in color when dried. Currie finds that heating has little visible effect on the compound until temperatures around 100° are reached, when a dulling of the color is noted. At 135° the pigment darkens appreciably to a brown and at 150° traces of black appear, indicating decomposition with the formation of black trisulfide. Carbon bisulfide, chloroform, carbon tetrachloride, benzene, and toluene are without influence on the pure pentasulfide in the cold and have little effect at the boiling points of the several solvents, even in the case of carbon bisulfide.⁷ Heating the sulfide causes it to lose sulfur to carbon bisulfide in amounts depending on the temperature. If heated between 70 and 75° it loses 1 atom of sulfur, leaving antimony

¹ *Z. anal. Chem.*, **30**, 428 (1891).

² *Compt. rend.*, **123**, 54 (1896).

³ *Liebig's Ann.*, **263**, 371 (1891).

⁴ BRAUNER and TOMICEK: *J. Chem. Soc.*, **53**, 145 (1888).

⁵ *J. Chem. Soc.*, **67**, 515 (1895).

⁶ CURRIE: *J. Phys. Chem.*, **30**, 205 (1926).

⁷ KLENKER: *J. prakt. Chem.*, [2] **59**, 150 (1899); ESCH and BALLA: *Chem. Ztg.*, **28**, 595 (1904).

tetrasulfide, Sb_2S_4 , which starts to decompose slightly at 105° and rapidly at 155 to 160° giving Sb_2S_3 .¹ Light acts slowly on the orange compound, converting it into black trisulfide.²

What is claimed to be the best method of preparing antimony pentasulfide is to treat a solution of Schlippe's salt, $Na_3SbS_4 \cdot 9H_2O$, with dilute acids.³ The product is never pure, containing, according to Klenker, Sb_2S_5 , Sb_2S_3 , and S in varying amounts, depending on the experimental conditions. This view was called in question by Kirchhof⁴ and by Short and Sharpe⁵ who claim that the so-called golden sulfide of antimony is the tetrasulfide, Sb_2S_4 . This question has been settled recently in Bancroft's laboratory by Currie,⁶ who examined the golden precipitates obtained from thioantimonate under different conditions. Equal samples of the several preparations were treated with increasing amounts of sulfur solvent and allowed to stand at constant temperature until equilibrium was reached. The concentration of sulfur in the solution and the composition of the residue were determined. Plotting concentration of sulfur in solution against the composition of the residue expressed in milligrams of S in excess of Sb_2S_3 , curves were obtained which indicate that the decomposition of thioantimonate by dilute acids yields no antimony pentasulfide, but a mixture of sulfur and a solid solution of sulfur and antimony tetrasulfide.

Heating trisulfide with sulfur yields neither tetrasulfide nor pentasulfide.⁷ Moreover, the trisulfide does not take up sulfur when kept in contact with sulfur solvents saturated with sulfur. It appears, therefore, that the equilibria $Sb_2S_5 \rightleftharpoons Sb_2S_3 + 2S$ and $Sb_2S_4 \rightleftharpoons Sb_2S_3 + S$ can be approached from one direction only, the side corresponding to the higher sulfide. The reason for this is not obvious.

¹ KLENKER: *loc. cit.*; LUFF and PORRITT: *J. Soc. Chem. Ind.*, **40**, 275 T (1921); DUBOSC: "Le Caoutchouc et la Gutta Percha," 8886, 8958 (1916).

² BRAUNER: *J. Chem. Soc.*, **67**, 528 (1895).

³ ABEGG: "Handbuch anorg. Chem.," **3**, (3) 620 (1907).

⁴ Z. anorg. Chem., **112**, 67; **114**, 266 (1920).

⁵ J. Soc. Chem. Ind., **41**, 109 T (1922); cf., however, TWISS: *Ibid.*, **41**, 171 T (1922).

⁶ J. Phys. Chem., **30**, 209 (1926).

⁷ CURRIE: *J. Phys. Chem.*, **30**, 216 (1926).

X-radiograms of pure pentasulfide and of the tetrasulfide from antimonate show no indication of crystalline structure and they are probably amorphous bodies.¹ A sol of the tetrasulfide from Schlippe's salt has been prepared using sodium "protalbinate" as a protective colloid. This sol can be sterilized by boiling and is recommended as a veterinary remedy in place of the antimonate.²

The golden sulfide is widely employed as a pigment for rubber and as an assistant in the vulcanization process. These applications are considered in Chap. VII.

COLLOIDAL BISMUTH TRISULFIDE

Bismuth trisulfide is thrown down as a brownish black hydrous mass on passing hydrogen sulfide into a solution of bismuth chloride that is not too strongly acid. No precipitate is obtained if the concentration is greater than 12 per cent HCl and is incomplete in solutions stronger than 7.7 per cent HCl.³ The sulfide is also precipitated from a bismuth chloride solution by sodium thiosulfate⁴ and by thioacetic acid.⁵ Adsorbed water is not removed completely from the sulfide until a temperature of approximately 200° is reached. Bismuth ion may be precipitated and weighed quantitatively as Bi₂S₃ provided the sulfide is heated for 1 hour in a stream of hydrogen sulfide.⁶ At this temperature the amorphous powder goes over rapidly to the crystalline form.⁷ Bismuth trisulfide is much less soluble in alkali sulfides than the corresponding sulfides of arsenic and antimony⁸ but the solubility is not inappreciable.⁹

A bismuth trisulfide sol results on passing hydrogen sulfide into a dilute solution of bismuth salt and dialyzing to remove

¹ CURRIE: *J. Phys. Chem.*, **30**, 237 (1926).

² WOLVEKAMP: U. S. Patent, 1412438 (1922).

³ RAMACHANDRAN: *Chem. News*, **131**, 135 (1925).

⁴ VORTMANN: *Monatsh.*, **7**, 418 (1886).

⁵ TARUGI: *Gazz. chim. ital.*, **27**, I, 316 (1897).

⁶ MOSER and NEUSSER: *Chem. Ztg.*, **47**, 541, 581 (1923).

⁷ SPRING: *Z. physik. Chem.*, **18**, 553 (1895).

⁸ STONE: *J. Am. Chem. Soc.*, **18**, 1091 (1896).

⁹ DITTE: *Compt. rend.*, **120**, 186 (1895); STILLMAN: *J. Am. Chem. Soc.*, **18**, 683 (1896).

excess electrolyte. Winssinger¹ employed a dilute bismuth nitrate solution treated with acetic acid and dialyzed 36 hours. The sol could be boiled without precipitation but was quite sensitive to the action of electrolytes. In thin layers the color was reddish brown and gave an absorption spectrum extending from the violet to the green and faintly into the red. Ozone precipitated the sol but was without action on the sulfide.²

Schneider³ claims to get a hydrate of bismuth monosulfide, $\text{BiS} \cdot \text{H}_2\text{O}$, by treating a solution of bismuth tartrate, stannous chloride, and potassium hydroxide with hydrogen sulfide; but Vanino and Treubert⁴ showed that the alleged compound was a mixture of hydrous bismuth trisulfide and bismuth. There appears to be no conclusive evidence of the existence of any sulfide of bismuth other than the trisulfide.⁵

COLLOIDAL STANNIC SULFIDE

Stannic sulfide is precipitated as a yellow gel by the action of hydrogen sulfide on an acidified solution of stannic chloride. The precipitate contains no stannous sulfide, but may contain hydrous stannic oxide owing to hydrolysis of the chloride in case the solution is quite dilute or but slightly acid.⁶ It is probable that any oxide carried down would be converted to sulfide by prolonged action of hydrogen sulfide, since the gas converts a suspension of freshly formed stannic oxide into sulfide.⁷ Stannic oxide sol peptized by hydrochloric acid, is coagulated by hydrogen sulfide but in this case the conversion to stannic sulfide is quite slow⁸ because of the physical character of the oxide.

¹ *Bull. acad. roy. méd. Belg.*, [3] **15**, 390 (1888); *Bull. soc. chim.*, [2] **49**, 452 (1888).

² RIESENFELD and HAASE: *Z. anorg. Chem.*, **147**, 188 (1925).

³ *Pogg. Ann.*, **97**, 480 (1856).

⁴ *Ber.*, **32**, 1079 (1899).

⁵ ATEN: *Z. anorg. Chem.*, **47**, 386 (1905); HERZ and GUTTMANN: *Z. anorg. Chem.*, **53**, 63 (1907); **56**, 422 (1908); cf., however, PÉLALON: *J. chim. phys.*, **2**, 321 (1904); *Compt. rend.*, **137**, 648, 920 (1903).

⁶ STORCH: *Monatsh.*, **10**, 260 (1889).

⁷ SCHEERER: *J. prakt. Chem.*, [2] **3**, 472 (1871).

⁸ JÖRGENSEN: *Z. anorg. Chem.*, **28**, 140 (1901); BARFOED: *J. prakt. Chem.*, **101**, 368 (1867).

The adsorbing power of stannic sulfide renders it unsuitable for the quantitative analysis of certain solutions. Thus cobalt and nickel are carried down by the gel, the amount adsorbed varying inversely as the hydrogen ion concentration of the solutions.¹ The gel also adsorbs phosphate so strongly² that quite low results are obtained when the phosphate is estimated after the removal of tin as sulfide.³

A sol of stannic sulfide was first prepared in 1839 by the action of sulfur dioxide on a dilute acidified solution of stannous chloride.⁴ More recently Schneider⁵ obtained a sulfide sol by passing hydrogen sulfide into a dilute sol of hydrous stannic oxide formed by dialysis of a stannic chloride solution. The sol was coagulated by a drop of acid giving a yellow gelatinous mass. Probably the most satisfactory method of preparing the sol is to peptize the freshly precipitated gel by thorough washing.

If a stannic sulfide gel is allowed to remain in contact with ammonia, a solution results from which a voluminous white precipitate is obtained on acidification.⁶ The same substance is formed by digesting stannic sulfide with ammonium carbonate solution, filtering, and acidifying. The dark red solution of stannous sulfide in ammonia becomes colorless on standing in the air and from this also, the white voluminous gel is precipitated by an acid. When freed from sulfur by washing with carbon bisulfide the precipitate analyzes for hydrous stannic oxysulfide, $\text{Sn}_2\text{S}_3\text{O} \cdot x\text{H}_2\text{O}$. The freshly formed gel is readily soluble in ammonium carbonate but when aged by drying, it loses this property to some extent. If a dilute solution of the gel in ammonium carbonate is acidified with sulfuric acid and shaken until most of the carbon dioxide is removed, there results a very fine flocculent mass with a blue tinge. On washing with water, this gel is peptized, giving a sol with an acid reaction. Schmidt attributes the acidity of the sol to the presence of an acid, $\text{Sn}_2\text{S}_3\text{O} \cdot \text{H}_2\text{O}$ or $\text{S}(\text{SnS} \cdot \text{OH})_2$. It seems more likely that the acid reaction

¹ AUGER and ODINOT: *Compt. rend.*, **178**, 710 (1924).

² KIKUCHI: *J. Chem. Soc. Japan*, **43**, 329 (1922).

³ LORD: *Chem. News*, **118**, 254 (1919).

⁴ HERRING: *Ann. Pharm.*, **22**, 90 (1839).

⁵ Z. *anorg. Chem.*, **5**, 83 (1894).

⁶ SCHMIDT: *Kolloid-Z.*, **1**, 129 (1906).

is due to the presence of some sulfuric acid which can not be washed out before peptization of the gel takes place.

COLLOIDAL LEAD SULFIDE

Hydrogen sulfide precipitates lead sulfide as a brownish-black powder from slightly acid, neutral, or alkaline solutions of lead salts. If the solutions are highly diluted, the sulfide does not precipitate out but forms a fairly stable sol which may be purified to some extent by dialysis.¹ The use of the sol for the colorimetric estimation of small amounts of lead has been recommended.² A fairly stable sol may be formed by the cathodic disintegration of galena;³ but if sols of a high degree of stability are desired, some protective colloid must be used. Lefort and Thibault⁴ added hydrogen sulfide to a solution of lead acetate containing gum arabic and Menegazzi⁵ used such protective colloids as peptone, white of egg, and starch paste. Lewis and Waumsley⁶ prepared a deep brown opalescent sol by allowing lead to remain in contact with a solution of caoutchouc in 90 per cent commercial benzene containing a small amount of carbon bisulfide. The carbon bisulfide acts on the lead, giving lead sulfide, which is protected by the caoutchouc. Any zinc or lead sulfide formed during the vulcanization of rubber in the presence of the metallic oxides, is kept in the colloidal state by the rubber.⁷

¹ WINSSINGER: *Bull. soc. chim.*, [2] **49**, 452 (1888).

² LUCAS: *Bull. soc. chim.*, [3] **15**, 39 (1896); WILLIAMS: *J. Soc. Chem. Ind.*, **25**, 137 (1906); EWAN: *Ibid.*, **28**, 10 (1909); HARCOURT: *J. Chem. Soc.*, **97**, 841 (1910).

³ VON HAHN: *Kolloid-Z. (Zsigmondy Festschrift)* **36**, 277 (1925).

⁴ *J. pharm. chim.*, [5] **6**, 169 (1882).

⁵ *J. Chem. Soc.* **110**, (1), 452 (1916).

⁶ *Kolloid-Z.*, **11**, 39 (1912); *J. Soc. Chem. Ind.*, **31**, 518 (1912).

⁷ MARTIN and DAVEY: *J. Soc. Chem. Ind.*, **45**, 174 T (1926).

CHAPTER IV

THE COLLOIDAL SULFIDES OF COPPER, SILVER, AND GOLD

COLLOIDAL CUPRIC SULFIDE

The precipitate obtained by the action of hydrogen sulfide on a solution of cupric salt is not pure cupric sulfide as usually supposed. Thus, if the gas is conducted into a solution of cupric sulfate or chloride, the precipitate is a mixture of Cu_2S , CuS , and S , according to Brauner,¹ and a mixture of Cu_4S_3 and S according to Thomsen.² Coppock³ found, however, that if copper sulfate, weakly acidified with nitric acid, is added in slight excess to a solution of hydrogen sulfide, no reduction takes place, the precipitate having the composition CuS after washing with hydrogen sulfide water, alcohol, and carbon bisulfide and dried at 100° . Antony and Lucchesi⁴ claim to get a pure product by precipitation and washing at 0° in an atmosphere of hydrogen sulfide and drying at 120° in a current of nitrogen.

The gel of copper sulfide adsorbs hydrogen sulfide strongly, a circumstance which led Linder and Picton to conclude that hydro-sulfides are formed, such as $7\text{CuS} \cdot \text{H}_2\text{S}$ and $9\text{CuS} \cdot \text{H}_2\text{S}$. The sulfide thrown down by alkali sulfides is always contaminated more or less by adsorbed alkali salt.⁵ If precipitated in the presence of zinc, the latter is adsorbed in amounts depending on the concentration of zinc salt, the concentration of acid, and the temperature.⁶ For the quantitative separation of copper and zinc, the acid should be 0.5 normal. Kolthoff and van Dijk⁷ claim that the precipitation of copper sulfide in the presence of

¹ *Chem. News*, **74**, 99 (1896); cf. ABEL: *Z. anorg. Chem.*, **26**, 411 (1901).

² *Ber.*, **11**, 2043 (1878).

³ *Chem. News*, **73**, 262 (1896); **76**, 231 (1897).

⁴ *Gazz. chim. ital.*, **19**, 545 (1890).

⁵ MURMANN: *Monatsh.*, **17**, 706 (1896); SCHERINGA: *Pharm. Weekblad.*, **57**, 1294 (1920).

⁶ SCHERINGA: *Pharm. Weekblad.*, **55**, 431 (1918).

⁷ *Pharm. Weekblad.*, **59**, 1351 (1922).

zinc should be carried out in the cold if sulfuric acid is employed and in the hot if hydrochloric acid is used. The reason for this is not obvious, for one should expect to get less contamination at higher temperatures in each instance, both because adsorption falls off with increasing temperature and because the precipitate is more granular the higher the temperature of formation. Schering¹ believes that the zinc is not adsorbed superficially but that zinc sulfide forms a solid solution with cupric sulfide at the moment of precipitation. Since the amorphous flocculent mass can be converted into the crystalline form by heating in vacuum² or with an ammonium sulfide solution,³ the question as to whether the mixture is a solid solution or an adsorption complex could be determined by x-ray analysis.

A very finely divided copper sulfide results on placing copper and sulfur in contact in a slightly acid solution of a copper salt.⁴ The sulfide is soluble in sulfuric acid yielding hydrogen sulfide.⁵

Solid cupric sulfide is a relatively good conductor of electricity, Bädeker⁶ finding the specific resistance at ordinary temperature to be 0.000125 when that of copper is 0.0000017 and that of bismuth is 0.000115.⁷ Thus cupric sulfide is almost as good a conductor as bismuth. Hittorf⁸ and Bodländer and Idaszewsky⁹ observed no migration of copper ions during the passage of the current and concluded therefore that the salt conducts like a metal and not like an electrolyte. Cuprous sulfide is, likewise, a conductor but the bulk of the evidence indicates that it conducts electrolytically.¹⁰ Bodländer attributes the slight conductivity

¹ *Pharm. Weekblad.*, **55**, 431 (1918).

² STANEK: *Z. anorg. Chem.*, **17**, 118 (1898).

³ SPRING: *Z. physik. Chem.*, **18**, 557 (1895).

⁴ WICKE: *Liebig's Ann.*, **81**, 241 (1852); GARELLI: *Rec. trav. chim.*, **42**, 818 (1923).

⁵ RIEDER: *Z. Elektrochem.*, **8**, 370 (1902).

⁶ *Ann. Physik*, [4] **22**, 749 (1907).

⁷ GIEBE: Dissertation, Berlin (1903).

⁸ *Pogg. Ann.*, **84**, 1 (1851).

⁹ *Z. Elektrochem.*, **11**, 161 (1905).

¹⁰ HITTORF: *Pogg. Ann.*, **84**, 1 (1851); KOHLRATSCH: *Wied. Ann.*, **17**, 642 (1883); BIDWELL: *Phil. Mag.*, [5] **20**, 322 (1885); MÖNCH: *Neues Jahrb. Min.*, **20**, 365 (1905); THOMPSON: *Z. anorg. Chem.*, **32**, 365 (1905); VON HASSLINGER: *Monatsh.*, **28**, 173 (1907); TRÜMPFER: *Z. physik. Chem.*, **99**, 9 (1921); TUBANDT, EGGERT, and SCHIBBE: *Z. anorg. Chem.*, **117**, 1 (1921).

of cuprous sulfide at room temperature to the presence of a small amount of cupric sulfide. He states further that at 110°, cuprous sulfide becomes an electrolyte but the electrolysis produces cupric sulfide at the anode, the metallic conductivity of the latter gradually replacing the electrolytic conductivity of the former.

A satisfactory explanation of metallic conduction in compounds such as cupric sulfide is not yet available. Trümpler¹ measured the potential of a number of solid conducting salts against a saturated solution containing the negative component of the salt in the free and ionic state. From the different behavior of metal-like and electrolytic conductors with respect to the influence of the negative component on the potential, a fundamental difference in internal structure is deduced. Thus it is assumed that in pure metallically conducting compounds, the space lattice points are occupied by atoms or molecules but not by ions; hence such compounds appear to be non-polar, in contradistinction to electrolytic conductors. While this assumption may be true, it is not very helpful for it offers no explanation of the fact that metallic conductivity obtains with only a few salts. Moreover, it does not account for the very much greater metallic conductivity of cupric sulfide than other salts of the same kind. Since Bridgman² has prepared a modification of phosphorus possessing metallic properties, it may be that a similar form of sulfur exists and that cupric sulfide is a compound of copper with this metallic form of sulfur.

Precipitated cupric sulfide is black, bluish black, greenish black, or brown depending on the conditions of formation. If thrown down by hydrogen sulfide from a cold cupric salt solution it is quite brown while the product from a hot solution has a greenish tinge.³ The crystalline mineral is black, bluish black, indigo blue, dark violet, or brown. The precipitated sulfide, submitted to a pressure of 6500 atmospheres, forms a mass with a deep blue metallic luster.⁴

¹ *Z. physik. Chem.*, **99**, 9 (1921).

² *J. Am. Chem. Soc.*, **36**, 1344, (1914); **38**, 609 (1916).

³ LOTTERMOSER: *J. prakt. Chem.*, [2] **75**, 293 (1907).

⁴ SPRING: *Bull. acad. roy. méd. Belg.*, [3] **5**, 492 (1883).

If copper nitrate solution is placed in a cracked test tube immersed in a beaker of sodium sulfide solution, keeping the two liquids at the same level, copper sulfide first forms in the cracks and is followed by the appearance of crystals of copper on the copper nitrate side and of a yellow layer of solution containing polysulfide on the other side. Becquerel,¹ who first observed this phenomenon, believed it to be connected in some way with electroendosmose.² Thirty years after Becquerel's discovery Braun³ passed a high-potential current through capillaries such as cracked glass, using heavy metal solutions, and observed a deposition of metal on the side of the capillary turned toward the positive pole. This phenomenon, called "electrostenolysis," is similar in certain respects to the Becquerel phenomenon and Coehn⁴ believes it to be closely connected with electroendosmose.

It is well known that colloidal particles will migrate in an electric field in a direction depending on their charge. This is known as cataphoresis. If the particles are kept stationary, in other words, if a porous diaphragm of the particles separates the anodic and cathodic solution, an impressed potential will cause the liquid to move in a direction depending on the sign of the diaphragm charge which, in turn, depends on the nature of the ion preferentially adsorbed by the diaphragm.⁵ This phenomenon is called electroendosmose. The inner walls of the capillary in contact with the liquid is coated with an electrical double layer. With a glass capillary, the stationary layer on the glass is negatively charged, as a rule, owing to preferential adsorption of anions, while the movable layer in the liquid contains an excess of cations and so is positively charged. Under the influence of an electric current of sufficient voltage, the positively charged movable side of the double layer is torn away, leaving the end of

¹ *Compt. rend.*, **64**, 919, 1211; **65**, 51, 720 (1867); **66**, 77, 245, 766, 1066; **67**, 1081 (1868); **71**, 197 (1870); **74**, 1310 (1872); **76**, 245 (1873); **78**, 1081; **79**, 82, 1281 (1874); **80**, 585 (1875); **82**, 354 (1876); **84**, 145; **85**, 169 (1877).

² Cf., however, OSTWALD: *Z. physik. Chem.*, **6**, 71 (1890).

³ *Ann. chim. phys.*, **42**, 450 (1891); **44**, 473 (1892).

⁴ Z. *Elektrochem.*, **4**, 501 (1898); Z. *physik. Chem.*, **25**, 651 (1898); HOLMES: *J. Am. Chem. Soc.*, **36**, 784 (1914).

⁵ PERRIN: *J. chim. phys.*, **2**, 601 (1904); BETHE and TOROPOFF: *Z. physik. Chem.*, **88**, 686 (1914); **89**, 597 (1915); GIRARD: *J. chim. phys.* **17**, 383 (1919); GYEMANT: *Kolloid-Z.*, **28**, 103 (1921).

the capillaries toward the anode charged negatively. On these cathodic points metals will deposit only in small amounts as a rule; first, because of the relatively small charge on the capillary wall and, second, because the minute deposit takes part in the conduction, one end becoming anode and losing as fast as the cathode end gains. But as Coehn points out, the quantity of metal can grow under certain conditions: first, if the metal is noble; second, if an insoluble compound, especially a peroxide, is formed at the anode side; and third, if the discharged anion instead of dissolving the metal, oxidizes "ous" to "ic" salts in the solution.

In Becquerel's experiment, Freundlich¹ points out that the two sides of the glass capillary will be oppositely charged by contact with the oxidizing and reducing solutions on the two sides. Now, as already noted, copper sulfide is first formed in the capillary and this salt is a fairly good metallic conductor. Local currents will therefore be formed which flow in one direction through the capillaries and in the opposite direction through the copper sulfide as well. Just as in the case of electrostenolysis, an appreciable amount of metal can form on the cathodic portion of the capillary provided the conditions referred to above obtain.

Rhythmic bands of cupric sulfide are formed when copper ion is allowed to diffuse into a gelatin jelly containing ammonium polysulfide.² The bands are white in color at the outset but they gradually become darker, changing through green to brown. It seems unlikely that cupric sulfide should be white and the initial white precipitate is doubtless sulfur. It is not observed if ammonium sulfide is substituted for the polysulfide.

Liesegang³ placed a strong sodium chloride solution containing a little sodium sulfide in the bottom of a beaker; over this was placed a more dilute sodium chloride solution and finally a layer of very dilute cupric sulfate solution. After a time, the copper ion diffusing downward and the sulfur ion upward come in contact and form a thin layer of cupric sulfide which gradually settles down. A process similar to this is believed to account for

¹ "Kapillarchemie," 371 (1922).

² HAUSMANN: *Z. anorg. Chem.*, **40**, 123 (1904).

³ *Z. angew. Chem.*, **36**, 229 (1923).

the copper sulfide deposit in certain lakes. In the salt water at the bottom of the lake, hydrogen sulfide is formed by the decay of organisms and by sulfur bacteria. During a flood, fresh water containing a little copper ion flows over this salt water. By diffusion, there is formed gradually a layer of copper sulfide which settles slowly to the floor of the lake.

Various polysulfides of copper have been described having the formulas, CuS_3 ,¹ Cu_4S_5 , Cu_2S_3 , and Cu_2S_5 ,² but the experimental evidence for their existence is altogether inconclusive.

CUPRIC SULFIDE SOLS

Hydrosols.—Colloidal cupric sulfide was first mentioned by Wright³ who prepared it by treating the precipitated salt with insufficient potassium cyanide for complete solution, filtering and washing the residue which was promptly peptized. Spring⁴ first obtained a stable sol by washing the precipitated sulfide with hydrogen sulfide water until peptization was complete. The sol was brown when dilute and black with a slight greenish fluorescence when concentrated. It withstood boiling without precipitation but was quite sensitive to the presence of salts. The amorphous residue obtained on evaporating to dryness had the appearance of a black varnish. The dry sulfide was not peptized by washing even when the drying was done at ordinary temperatures. Linder and Pieton⁵ suspended hydrous cupric oxide in water through which hydrogen sulfide was passed until the oxide was converted into sulfide and peptization was complete, 5 days being required. Young and Neal⁶ started with suspended copper carbonate instead of the hydrous oxide.

Muthmann and Stützel⁷ made a fairly stable sol by passing hydrogen sulfide into a solution of potassium cupri thiosulfate, $\text{K}_2\text{Cu}(\text{S}_2\text{O}_3)_2$. Lottermoser⁸ obtained a very much more satis-

¹ RÖSSING: *Z. anorg. Chem.*, **25**, 407 (1900).

² BODROUX: *Compt. rend.*, **130**, 1397 (1900).

³ *J. Chem. Soc.*, **43**, 163 (1883).

⁴ *Ber.*, **16**, 1142 (1883).

⁵ *J. Chem. Soc.*, **61**, 120 (1892).

⁶ *J. Phys. Chem.*, **21**, 14 (1917).

⁷ *Ber.*, **31**, 1734 (1898).

⁸ *J. prakt. Chem.*, [2] **75**, 293 (1907).

factory preparation by treating a saturated solution of copper glycocoll with hydrogen sulfide. When the procedure was carried out in the cold, the sol was clear brown in color and was made up of very finely divided particles; when carried out in the boiling solution, the color was a deep olive green and the particles were distinctly larger. The brown sol formed in the cold was changed to green by heating. The presence of glycocoll has a marked stabilizing influence on the sol, just as succinimide protects hydrous cupric oxide sol when the latter is formed by hydrolysis of copper succinimide.¹

The removal of the excess hydrogen sulfide from sols prepared by the method of Spring or of Linder and Pierton, decreases their stability appreciably.² On the other hand, an excess of hydrogen sulfide is said to decrease the precipitation value of electrolytes for the sol.³ The relative precipitating powers of KCl, CaCl₂, and AlCl₃ are in the approximate ratio 1:39:875.

Peskov⁴ observed the same lyotrope influence of the cation of neutral alkali salts on the solution of colloidal cupric sulfide as already noted with colloidal arsenic trisulfide.⁵

Organosols.—Organosols of cupric sulfide are prepared by passing hydrogen sulfide through dilute solutions of copper salts in an organic solvent. Thus Naumann⁶ obtained a pyridine sol by the action of dry hydrogen sulfide on a dilute solution of copper chloride in pyridine; Lottermoser⁷ made an alcosol from a solution of copper glycocoll in absolute alcohol and an ether sol from a solution of copper acetoacetic ester in ether; and Errera⁸ prepared an alcosol from a solution of copper acetate in absolute alcohol. In general, the organosols are most stable when quite dilute but Errera's alcosol was quite stable although it contained 38.7 grams CuS per liter.

Errera observed the time required to coagulate alcosols of mercuric sulfide, cupric sulfide, and platinum by the addition of

¹ LEY: *Ber.*, **38**, 2199 (1905).

² YOUNG and NEAL: *J. Phys. Chem.*, **21**, 18 (1917).

³ MUKHERJEE and SEN: *J. Chem. Soc.*, **115**, 461 (1919).

⁴ *Kolloid-Z.*, **32**, 24, 163 (1923).

⁵ Cf. p. 23.

⁶ *Ber.*, **37**, 4612 (1904).

⁷ *J. prakt. Chem.*, [2] **75**, 293 (1907).

⁸ *Kolloid-Z.*, **32**, 240 (1923).

liquids of varying dielectric constant. One cubic centimeter of the alecosol containing 38.7 grams CuS per liter was added to 6-cubic centimeter portions of the several liquids and the observations made as recorded in Table XIV. Experiments were also carried out with mixtures of the several liquids with varying quantities of ethyl aleohol. The observations disclose that the addition of liquids having a dielectric constant greater than the dispersing medium has no coagulating effect on the sol, while liquids with a dielectric constant smaller than that of the dispersing medium coagulate the sols and, in most cases, the smaller the dielectric constant the greater is the coagulating power of the

TABLE XIV.—ACTION OF LIQUIDS ON CUPRIC SULFIDE ALCOSOL

Liquid	Dielectric constant	Observations
Water.....	81	Milky in 30 minutes, no further change in 127 hours
Nitrobenzol.....	35.5	No change in 127 hours
Methyl aleohol.....	33.0	No change in 127 hours
Ethyl aleohol.....	25.0	No change in 127 hours
Acetone.....	21.0	No change in 127 hours
Isobutyl aleohol.....	18.0	No change in 127 hours
Isoamyl aleohol.....	5.7	No change in 127 hours
Amyl acetate.....	5.6	No change in 127 hours
Chlorobenzene.....	5.57	Partial coagulation in 8 minutes; complete in 3.5 hours
Chloroform.....	4.95	Partial coagulation in 96 hours, incomplete in 126 hours
Ether.....	4.36	Partial coagulation in 10 minutes; complete in 3.5 hours
Benzol.....	2.29	Partial coagulation in 96 hours; incomplete in 126 hours
Xylo.....	2.5	Incomplete coagulation in 7 minutes; complete in 3.5 hours
Hexane.....	1.85	Complete in 1 minute
Carbon tetrachloride	2.25	Incomplete in 1 minute; complete in 3.5 hours

added liquid. In general, if the dielectric constant of the dispersed phase is greater than that of the dispersing liquid, the addition of a second liquid of lower dielectric constant increases

the difference between the dielectric constant of the two phases, thereby rendering the sol more stable. On the other hand, if the dispersed phase has the lower dielectric constant and if the dielectric constant of the medium is further decreased, two cases exist: (1) The difference in dielectric constant is slight, the initial additions decreasing the stability to a minimum followed by an increase in stability with further additions. (2) The dispersing phase may have a very low dielectric constant, additions decreasing the stability both by decreasing the difference between the dielectric constant of the media and by lowering the charge on the submierons. Cupric sulfide alcrosol, both alone and when mixed with ten times its volume of benzene, is negatively charged. Agglomeration of the colloidal particles is always accompanied by the distinct color change from dark brown to a bright olive green.

COLLOIDAL CUPROUS SULFIDE

When a solution of NaCuS_2O_3 is acidified, there is a period of induction followed by the appearance of red cuprous sulfide in colloidal solution.¹ This subsequently precipitates giving a blood-red gel which turns successively brown, deep brown, greenish black, and finally black. The length of the induction period depends on the nature and concentration of the acid and the concentration of NaCuS_2O_3 . The chief cause of the phenomenon is the formation of colloidal sulfur, which inhibits the precipitation process. The use of ozonized hydrochloric acid, nitric acid, or perchloric acid which oxidize colloidal sulfur, cuts down the induction period. With a constant amount of acid and NaCuS_2O_3 , the presence of increasing amounts of $\text{Na}_2\text{S}_2\text{O}_3$ decreases the induction period up to a certain point and then increases it. The hastening is attributed to the coagulating influence of the added salt on the colloidal sulfur; and the subsequent retarding at higher salt concentrations, to the destruction of acid.

Svedberg² prepared a sol of cuprous sulfide in isobutyl alcohol by electrical disintegration of the mineral, copper glance.

¹ SAMBAMURTZ: *Proc. Sci. Assocn. Maharajah's College, Vizianagram*, Dec. 10 (1922); *Chem. Zentr.*, I, 1414 (1923).

² "Die Methoden zur Herstellung kolloidaler Lösungen," 490 (1909).

COLLOIDAL SILVER SULFIDE

Silver sulfide is precipitated as a black amorphous powder by the action of hydrogen sulfide or a soluble sulfide on a solution of silver oxide or salt. The precipitate from neutral silver nitrate solution always contains adsorbed sulfur which cannot be removed by carbon bisulfide.¹ Hantzsch² claims to have prepared silver disulfide, Ag_2S_2 , as a brown amorphous powder by adding a solution of sulfur in carbon bisulfide to a solution of silver nitrate in benzonitrile. If solvents other than benzonitrile are used, silver sulfide is obtained. Since the failure of carbon bisulfide to extract sulfur from the alleged disulfide is the chief evidence in support of its chemical individuality, there may be some question whether it is a true compound or a solution of Ag_2S and S.

Silver sulfide is formed by the action of moist hydrogen sulfide on metallic silver. According to Gans³ the reaction proceeds rapidly at first, slows down after 200 hours, increases again after 500 hours, and then continues at approximately constant velocity. It is suggested tentatively that the decrease in velocity after 200 hours is due to the formation of a protective layer of amorphous sulfide which is subsequently ruptured or crystallizes, allowing the surface action to proceed more rapidly. This hypothesis should be tested experimentally by x-ray analysis of the protecting layer of sulfide.

Unlike cupric sulfide which is a pure metallic conductor, β -silver sulfide stable below 179° is a mixed conductor, about 80 per cent of the current being carried by silver ions and 20 per cent being conveyed as in a metallic conductor; the α modification, stable above 179°, is a pure electrolytic conductor.⁴

SILVER SULFIDE SOLS

The most stable hydrosols of silver sulfide are obtained by precipitating the salt in the presence of protective colloids such

¹ KOHLSCHÜTTER and EYDMANN: *Liebig's Ann.*, **390**, 347 (1912).

² Z. *anorg. Chem.*, **19**, 104 (1899).

³ Z. *physik. Chem.*, **109**, 49 (1924).

⁴ TUBANT, EGGERT, and SCHIBBE: Z. *anorg. Chem.*, **117**, 1 (1921); cf. TRÜMPLER: Z. *physik. Chem.*, **99**, 9 (1921).

as gum arabic,¹ casein,² albumin, dextrin, gelatin, and glue.³ Paal and Voss⁴ prepared very stable sols using a salt of protalbinic or lysalbinic acid as protective colloid. One gram of sodium "protalbinate" in 15 cubic centimeters of water is treated with an equivalent amount of silver nitrate, the precipitate of silver "protalbinate" is suspended in water and treated with ammonium sulfide. The sol of silver sulfide which results is dialyzed to remove excess electrolyte and evaporated to dryness in a vacuum desiccator. The amorphous residue is readily peptized by water giving a stable sol of any desired strength.

A sol of silver sulfide is obtained without the use of a protective colloid by adding hydrogen sulfide to a dilute solution of silver nitrate.⁵ Lottermoser⁶ added a slight excess of *N*/40 sodium sulfide to *N*/40 silver nitrate.

Freundlich and Nathansohn⁷ obtained a silver sulfide sol by mixing Carey Lea's silver sol with a sulfur sol. Both of the sols are negatively charged and the interaction takes place between the micelles. The transformation is accompanied by a change in colors: brown, wine red, violet, steel blue, greenish blue, greenish brown, and finally a pale yellowish brown. The color changes are probably due to micelles with varying amounts of silver, sulfur, and silver sulfide, as in the case of the photo-chlorides.⁸ A mixture of a solution of hydrogen sulfide and colloidal silver goes through similar color changes, finally giving colloidal silver sulfide.

By passing hydrogen sulfide into a solution of silver nitrate as dilute as 0.002 normal a stable yellow sol of silver sulfide results.⁹ The fresh sol passes through a range of colors from yellow to green on adding electrolytes.¹⁰ Some observations of this phenomena are given in Table XV. Portions of 5 cubic centi-

¹ LEFORT and THIBAULT: *J. pharm. chim.*, [5] **6**, 169 (1882).

² MÜLLER and ARTMANN: *Oesterr. Chem. Ztg.*, **7**, 149 (1904).

³ STIASNY: *Gerber.*, **33**, 124 (1907); *Chem. Zentr.*, II, 489 (1907).

⁴ *Ber.*, **37**, 3862 (1904).

⁵ WINSSINGER: *Bull. soc. chim.*, [2] **49**, 452 (1888).

⁶ *J. prakt. Chem.*, [2] **72**, 39 (1905).

⁷ *Kolloid-Z.*, **29**, 16 (1921).

⁸ Cf. p. 226.

⁹ ODÉN: *Nova. acta. Upsala*, [4] **3**, 4 (1913).

¹⁰ VON HAHN: *Kolloid-Z.*, **27**, 172 (1920).

meters each of the colloid were mixed with 5 cubic centimeters of electrolytes of varying concentrations, and the color of each was noted after standing 5 minutes. The concentration of electrolyte is given in milliequivalents per liter in the final mixture. It will be noted that the color depends on the concentration of elec-

TABLE XV.—COLOR CHANGES IN THE COAGULATION OF SILVER SULFIDE SOL BY ELECTROLYSIS

(Concentration in milliequivalents per liter)

KCl		HCl		KNO ₃	
Concen- tration	Color	Concen- tration	Color	Concen- tration	Color
60	Yellow	80	Yellow	60	Dull green
80	Ice blue	100	Blue	80	Ice blue
90	Blue	120	Violet	100	Violet
100	Violet	140	Dull green	120	Brown red

MgSO		Al ₂ (SO ₄) ₃	
Concentration	Color	Concentration	Color
10	Yellow	1.5	Leaf green
20	Violet	2.4	Blue
40	Blue	3.0	Red
80	Dull green	3.6	Dull green

troyte between fixed limits. Thus, for potassium chloride there is no change below 60 milliequivalents per liter, and the color is always brownish red above 110 milliequivalents per liter. The stability at the above stages of agglomeration is not great and complete coagulation results in a few hours. The precipitate is always dark brown, but if shaken up with the solution from which it separates, the suspension appears bluish from the blue and violet sols and reddish from the red and dull green sols.

The age of the sol has a marked influence on the variety of the color changes during the flocculation of the sol. Thus, 5 hours after preparation no blue or green colors can be obtained; and

after 7 hours, no violet color. If allowed to stand 24 hours the sols change directly from yellow to reddish brown.

The results indicate that the micelles of the sol increase in size spontaneously at least during the first 24 hours. Secondary particles of a wide variety of sizes may be produced by partial agglomeration of fresh sols with varying amounts of electrolytes. The difference in size of the secondary aggregates is probably the chief cause for the wide variety of colors observed. It is a mistake, however, to conclude *a priori* that the variation in color is due entirely to the size of the micelles. Thus, colloidal gold sols¹ can be obtained which are red, violet, or blue by transmitted light; and colloidal silver sols² which are yellow, red, or blue. In general, the micelles of the blue sols are larger than the red but this is not always the case. Another factor which may come in is the property which metals have of showing selective reflections and the same may be true for the metallic sulfides. Where there is selective reflection, some or all of the light which is absorbed strongly by a substance is reflected strongly from a polished surface of the substance. For example, the surface color of indigo is red while the body color, which is due to transmitted light, is blue. The surface color is probably due to resonance, the substance emitting the rays which it absorbs strongly. In discussing this phenomenon Bancroft³ says:

It seems probable that a very small granular particle might emit surface color by resonance on the opposite side from the source of light, in which case we should have the surprising phenomenon of a substance apparently transmitting the light which it absorbs most strongly. On the other hand, the amount of reflection from the back surface of a particle of the light ordinarily transmitted will be greater the less the thickness of the particle. Consequently, with fine particles there will be a more or less complete reversal of the usual colors. The light which is ordinarily reflected selectively will be transmitted by resonance, while the light which is ordinarily transmitted is scattered.

Silver reflects yellow after multiple reflection, while with fewer reflections the light is said to be red.⁴ A very fine colloidal solution transmits yellow and scatters blue, while somewhat coarser particles transmit red

¹ FARADAY: *Phil. Trans.*, **147**, 145 (1857).

² LEA: *Am. J. Sci.*, [3] **37**, 475 (1889).

³ "Applied Colloid Chemistry," 252 (1926).

⁴ REGNAULT-BETTON: "Elements of Chemistry," 366 (1874).

and are blue by reflected light. The coarsest colloidal silver does not resonate and consequently is yellow by reflected light, transmitting blue light. This is exactly what should happen on the facts as stated.

There are no data to show what part if any of the color of colloidal silver sulfide sols is due to resonance.

The appearance of the violet color in the flocculation of fresh sols is so sharp that von Hahn¹ compared the stability of sols prepared under different conditions by means of the "violet value" which was taken arbitrarily as the concentration of electrolytes which is just sufficient to produce a certain shade of violet after 5 minutes standing (44 according to Ostwald's color scale). The stability of the sol was found to increase with (1) length of time of treatment with hydrogen sulfide, (2) more rapid passing of hydrogen sulfide through the solution, and (3) higher temperatures of formation. In general, the optimum conditions for stability are those which cause the maximum rate of precipitation and hence the greatest degree of dispersion. Von Hahn's observations agree with those of Bouterie and Vuillaume on arsenic trisulfide sol already referred to.²

The "violet value" for different electrolytes gives the order of their precipitating power. From Table XV the ratio $\text{Al}_2(\text{SO}_4)_3$: MgSO_4 : KCl : HCl is approximately 1:10:50:70.

Pieroni³ prepared a pyridine organosol of silver sulfide by treating a solution of silver nitrate in pyridine with hydrogen sulfide dissolved in pyridine.

COLLOIDAL SULFIDES OF GOLD

Gold Monosulfide. Gold monosulfide is formed by passing hydrogen sulfide into a solution of aurous cyanide in potassium cyanide and then acidifying with hydrochloric acid. The finely divided steel-gray mass must be washed with water containing dilute hydrochloric acid, otherwise it is peptized, forming a perfectly clear sol.⁴ When dried it yields a brownish-black powder that cannot be peptized. A sol is obtained also by saturating with hydrogen sulfide a solution of aurous cyanide in

¹ *Kolloid-Z.*, **29**, 139 (1921).

² Cf. p. 19.

³ PIERONI and TONNIOLI: *Gazz. chim. ital.*, [1] **43**, 198 (1913).

⁴ HOFFMANN and KRÜSS: *Ber.*, **20**, 2369 (1887).

potassium cyanide,¹ adding a little hydrochloric acid, and warming carefully until a brown turbidity is produced. On dialysis a stable deep-brown sol results which can be separated from the heavy undissolved sulfide by decantation and filtration.

Auro-auric Sulfide.—Auro-auric sulfide, Au_2S_2 , is said to form when hydrogen sulfide is passed into a cold neutral solution of auric chloride;² but Gutbier and Dürrwächter³ were unable to obtain the compound by this method and question its individuality. Whatever the substance may be it is readily obtained in colloidal solution. Thus Winssinger⁴ added hydrogen sulfide to a solution of auric chloride as nearly neutral as possible and secured a sol containing 0.55 gram of sulfide per liter which was stable for several weeks. Schneider⁵ made a more concentrated sol by treating the freshly precipitated sulfide with insufficient potassium cyanide or ammonium polysulfide for complete solution, suspending the residue in water, and dialyzing. After the electrolyte concentration was reduced below a critical value, the suspended particles were peptized, giving a stable sol that was clear in both transmitted and reflected light. The precipitate formed by agglomerating the sol was reddish brown when moist and black when dry.

An alcosol was prepared by mixing the hydrosol with three times its volume of alcohol, followed by dialyzing against absolute alcohol to remove the water. The alcosol was similar in appearance to the hydrosol but the former was more stable.

Gold Trisulfide.—On account of the alleged instability of Au_2S_3 in the presence of water, this salt was first prepared in the dry way or precipitated from non-aqueous media. Thus Antony and Lucchesi⁶ passed dry hydrogen sulfide over lithium auric chloride at -10° and Hofmann and Höchtlen⁷ precipitated the compound as a dark brown mass by the interaction of auric chloride and hydrogen sulfide in absolute ether. Gutbier and

¹ SCHNEIDER: *Ber.*, **24**, 2241 (1891).

² HOFFMANN and KRÜSS: *Ber.*, **20**, 2704 (1887); ANTONY and LUCCHESI: *Gazz. chim. ital.*, **19**, 545 (1890); DITTE: *Compt. rend.*, **120**, 320 (1895).

³ Z. *anorg. Chem.*, **121**, 266 (1922).

⁴ Bull. soc. chim., [2] **49**, 452 (1888).

⁵ Ber., **24**, 2241 (1891).

⁶ Gazz. chim. ital., **19**, 545 (1890).

⁷ Ber., **37**, 245 (1904).

Dürrwächter¹ claim to get Au_2S_3 instead of Au_2S_2 by passing a rapid stream of hydrogen sulfide into an aqueous solution of gold chloride at -2° . With a slow stream of hydrogen sulfide at 100° the trisulfide first formed reacts with the excess of gold chloride giving metallic gold. The precipitate obtained under intermediate conditions is said to be a mixture of Au_2S_3 and Au, no Au_2S_2 being formed by any modification of the procedure. These recent observations raise the question of the individuality of Au_2S_2 and suggest that the alleged Au_2S_2 precipitate and sol referred to in the preceding paragraph, are mixtures of Au_2S_3 and Au.

¹ *Z. anorg. Chem.*, **121**, 266 (1922).

CHAPTER V

THE COLLOIDAL SULFIDES OF ZINC, CADMIUM, AND MERCURY

COLLOIDAL ZINC SULFIDE

The gel of zinc sulfide is obtained by precipitating neutral, slightly acid, or alkaline solutions of zinc salts by hydrogen sulfide or alkali sulfides. The gel precipitated by hydrogen sulfide from a zinc sulfate solution at 0° is amorphous, the x-ray photograph showing only a broad band; but when the gel is digested for several days on the water bath, sharp interference lines show up, indicating that crystallization has taken place.¹ These crystals are submicroscopic since Allen, Crenshaw, and Merwin² found no microscopic evidence of crystalline structure in any gel precipitated and digested under ordinary laboratory conditions.³ Microscopic crystals are formed only by prolonged digestion of the gel in platinum tubes with sodium sulfide or sulfuric acid in the presence of an excess of hydrogen sulfide at temperatures varying from 200 to 350°. The crystals formed by digestion with sodium sulfide are always the common sphalerite or blende while both sphalerite and wurtzite are formed in the digestion with acid. At a given temperature the amount of wurtzite formed is greater the higher the acid concentration, and at a given acid concentration the amount of sphalerite is greater the higher the temperature.

Owing to the solubility of gelatinous zinc sulfide, the salt is not precipitated completely unless the hydrogen ion concentration is rather low. Allen, Crenshaw, and Merwin⁴ found, however, that

¹ BÖHM and NICLASSEN: *Z. anorg. Chem.*, **132**, 1 (1924).

² *Am. J. Sci.*, [4] **34**, 351 (1912).

³ Cf., however, BAUBIGNY: *Compt. rend.*, **143**, 678 (1906); VILLIERS: *Ibid.*, **120**, 149, 188, 498 (1895); STANEK: *Z. anorg. Chem.*, **17**, 117 (1898).

⁴ *Am. J. Sci.*, [4] **34**, 355 (1912); GLIXELLI: *Z. anorg. Chem.*, **55**, 297 (1907).

TABLE XVI.—ACTION OF H_2S AT 1 ATMOSPHERE ON 0.2 N $ZnSO_4$ WITH VARYING CONCENTRATIONS OF H_2SO_4

Normality of H_2SO_4		Approximate time before precipitation started	Zinc in solution after 10 days normality
Before precipitation	After precipitation		
0.1	0.300	1 minute	0.0000
0.2	0.398	5 minutes	0.0031
0.5	0.691	25 minutes	0.0089
1.0	1.183	a few hours	0.0338
1.5	1.609	3 days	0.0923

precipitation takes place on long standing from solutions which are quite strongly acid. This is shown by the data recorded in

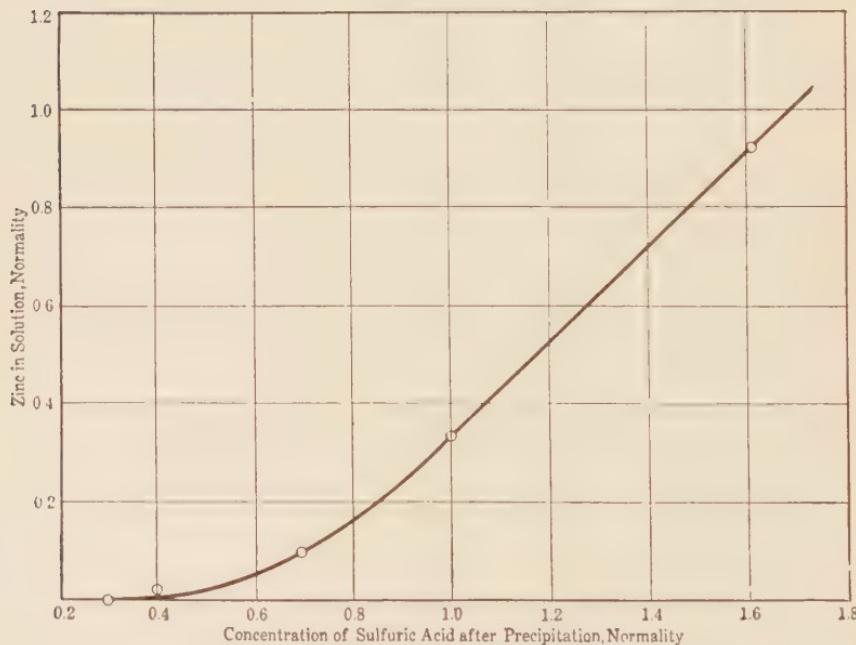


FIG. 8.—Influence of free acid on the precipitation of zinc sulfide.

Table XVI and shown graphically in Fig. 8. Thus precipitation is complete in 10 days or less from 0.3 normal H_2SO_4 and 98.5 per cent complete from 0.4 normal H_2SO_4 . The time interval before precipitation starts increases with increasing concentra-

tion of acid. In spite of the slowness with which the precipitate forms, the product is always a gel containing no microscopically visible crystals. On the other hand, the gel obtained by slow precipitation or by ageing contains much larger particles than a fresh, rapidly formed gel and the former is much less soluble than the latter.¹

In analytical practice the best hydrogen ion concentration for complete precipitation is between pH = 2 and pH = 3.² At lower pH values the precipitation is too slow or is incomplete and at values higher than pH = 3 the precipitation is so rapid that the slimy gel produced is very difficult to filter. Higher acid concentrations can be used, of course, provided the hydrogen sulfide pressure is increased.³ Quantitative precipitation is usually carried out in solutions of acetic acid (containing sodium acetate),⁴ tartaric acid,⁵ formic acid,⁶ thiocyanic acid,⁷ or dilute mineral acids. The precipitates are always so gelatinous that filtration is difficult or slow. To facilitate the process, Jander and Stuhlmann⁸ recommend the so-called membrane filters⁹ supplied by de Häen. Schilling¹⁰ claims to get more granular precipitates from a solution containing benzene sulfonic acid.

A zinc sulfide gel is obtained by the action of sodium thiosulfate on a solution of zinc salt in the cold or at 100°,¹¹ and by the alternating-current electrolysis of sodium thiosulfate solution with zinc electrodes.¹² It is also formed by direct-current elec-

¹ BRUNI and ZAWADSKI: *Bull. acad. Krakow*, 296 (1909); *Z. anorg. Chem.*, **65**, 136 (1910); BRUNI and PADOA: *Atti accad. Lincei*, [5] **14**, II, 525 (1905).

² FALES and WARE: *J. Am. Chem. Soc.*, **41**, 488 (1919).

³ BRUNI and PADOA: *Atti accad. Lincei*, [5] **14**, II, 525 (1905).

⁴ VILLIERS: *Compt. rend.*, **108**, 236 (1889).

⁵ ALT and SCHULZE: *Ber.*, **22**, 3259 (1889).

⁶ FALES and WARE: *J. Am. Chem. Soc.*, **41**, 487 (1919).

⁷ ZIMMERMANN: *Liebig's Ann.*, **199**, 1 (1819).

⁸ Z. anal. Chem., **60**, 289 (1921); cf., also, MOSER and KITTL: *Chem. Ztg.*, **44**, 637 (1920).

⁹ ZSIGMONDY and BACHMANN: *Z. anorg. Chem.*, **103**, 119 (1918); ZSIGMONDY and JANDER: *Z. anal. Chem.*, **58**, 241 (1919); JANDER and JANDER: *Ibid.*, **63**, 273 (1923).

¹⁰ *Chem. Ztg.*, **36**, 1352 (1912).

¹¹ ALLEN, CRENSHAW, and MERWIN: *Am. J. Sci.*, [4] **34**, 351 (1912).

¹² LE BLANC and SCHICK: *Z. physik. Chem.*, **46**, 213 (1903).

trolysis of an ammonium chloride solution using a zinc cathode and an anode of zinc coated with sulfur.¹

The freshly formed gel of zinc sulfide contains a great deal of adsorbed water. If dried under suitable conditions, compositions corresponding to hydrates such as $2\text{ZnS} \cdot \text{H}_2\text{O}$, $3\text{ZnS} \cdot \text{H}_2\text{O}$, $4\text{ZnS} \cdot \text{H}_2\text{O}$, $3\text{ZnS} \cdot 2\text{H}_2\text{O}$, and $\text{ZnS} \cdot \text{H}_2\text{O}$ can be obtained but it is probable that each one is merely a hydrous sulfide whose composition is the accidental result of the conditions of drying.

Zinc sulfide is a valued white pigment, both alone and when mixed with barium sulfate to give the commercial product known as lithopone. Unless special precautions are taken in the preparation of the pigments, they darken on exposure to light. The formation of the technical products and the cause of the blackening in light are considered in Chap. VIII on Lithopone. The phosphorescence of zinc sulfide is also discussed in a separate chapter (p. 156).

Owing to the solubility of zinc sulfide in acid solution, fibers impregnated with the salt may be employed in the microchemical detection of a number of metals which give colored sulfides.² Chamot and Cole³ dipped swollen wool fibers alternately in zinc acetate, which is fairly strongly adsorbed by the fibers, and sodium sulfide, thereby obtaining fibers which are sensitive to 0.001 milligram of copper. To make the test, a drop of the unknown solution is placed on an object glass and acidified with a drop of dilute hydrochloric acid. Into the drop is placed a small piece of the impregnated wool fiber which is subsequently examined under the microscope for color change.

ZINC SULFIDE SOLS

A gel of zinc sulfide freshly formed in the cold is easily peptized by removing the adsorbed salts by washing.⁴ Even when precipitated hot and allowed to stand several hours, the quantitative analyst must have ammonium sulfide or ammonium

¹ GRIFFITH: German Patent, 332199 (1921); GMELIN: "Handbuch anorg. Chem.," [8] **32**, 196 (1924); cf. also JACOLLIOT: French Patent, 415605 (1910); *Chem. Abstr.*, **6**, 1884 (1912).

² EMICH and DONAU: *Liebig's Ann.*, **351**, 432 (1907).

³ *Ind. Eng. Chem.*, **10**, 48 (1918).

⁴ DONNINI: *Gazz. chim. ital.*, **24**, I, 219 (1894).

chloride in the wash water to prevent sol formation. For obtaining more concentrated sols, the gel is thrown down from an ammoniacal solution with hydrogen sulfide, washed by decantation and suspended in water through which hydrogen sulfide is passed until peptization is complete.¹ This procedure may be modified by suspending freshly precipitated hydrous zinc oxide in water into which hydrogen sulfide is conducted until the oxide is completely transformed into an opalescent zinc sulfide sol. The excess hydrogen sulfide may be removed by heating to boiling, but prolonged heating decreases the stability and may cause precipitation. In the latter event, repeptization can be effected by treating with hydrogen sulfide, but the process requires more time with the aged gel than with a freshly formed one.² The peptizing action of hydrogen sulfide increases with the pressure up to 1.5 to 2 atmospheres, above which it apparently decreases slightly.³

A pale opalescent sol is formed by the action of NaHS on a dilute solution of zinc sulfate.⁴ Müller⁵ was unsuccessful in an attempt to prepare a stable sol by the interaction of ammonium sulfide and zinc sulfate in the presence of a large amount of glycerin. The increased viscosity slows down the reaction but the sulfide precipitates as a gel after a few days. The stability of the sol is increased enormously if prepared in the presence of protective colloids, such as gum arabic⁶ and gelatin.⁷

An x-radiogram of a zinc sulfide sol prepared by Winssinger's method showed the colloidal particles to possess a crystalline structure.⁸ A dilute sol appears clear in transmitted light while a concentrated sol possesses an orange-red color and shows a bluish fluorescence. The gel which precipitates from the sol either spontaneously or by the action of electrolytes is not a

¹ WINSSINGER: *Bull. soc. chim.*, [2] **49**, 452 (1888).

² VILLIERS: *Compt. rend.*, **120**, 149, 188 (1895).

³ YOUNG and GODDARD: *J. Phys. Chem.*, **21**, 1 (1917).

⁴ THOMSON: *Ber.*, **11**, 2044 (1878); VON ZOTTA: *Monatsh.*, **10**, 807 (1899).

⁵ *Chem. Ztg.*, **28**, 357 (1904).

⁶ LEFORT and THIBAULT: *J. pharm. chim.*, [5] **6**, 169 (1882).

⁷ ALEXANDER: U. S. Patent, 1259708 (1918).

⁸ HABER: *Ber.*, **55B**, 1730 (1922).

hydrosulfide such as $7\text{ZnS} \cdot \text{H}_2\text{S}$ or $12\text{ZnS} \cdot \text{H}_2\text{S}$ ¹ but is zinc sulfide with adsorbed hydrogen sulfide.²

COLLOIDAL CADMIUM SULFIDE

A highly hydrous gel of cadmium sulfide is precipitated by the action of hydrogen sulfide or of alkali sulfides on a cold solution of a cadmium salt. Although the sulfide appears to be amorphous, an x-radiogram³ of the gel obtained at 0° shows broad interference bands and of the gel thrown down at room temperature gives fairly sharp interference rings, indicating that the tendency for cadmium sulfide to form submicroscopic crystals is more marked than for the corresponding zinc salt. Microscopic crystals are obtained by precipitation or digestion at higher temperatures. Thus a gel formed at 100° from a solution containing 1 gram of CdSO₄ in 50 cubic centimeters of 30 per cent H₂SO₄ contains some doubly refracting needles; and a gel precipitated from a solution containing 2 grams CdSO₄ in 20 cubic centimeters of 30 per cent H₂SO₄ gives crystals 0.5 millimeter long, identical with the mineral greenockite, after digestion in the mother liquor for 3 days at 180°.⁴ Similarly, a gel digested at 150 to 200° with ammonium sulfide, which has a slight solvent action, yields large crystals similar to greenockite.⁵

For complete precipitation of cadmium sulfide, the solution must be saturated with hydrogen sulfide since prolonged action of acids, even in the cold, dissolves appreciable amounts of the salt.⁶ The equilibrium constant of the reaction CdSO₄ + H₂S ⇌ CdS + H₂SO₄ from solubility determinations in approximately molar H₂SO₄ containing a very little H₂S is $k = 6.6 \times 10^{-6}$ for the sulfide from CdCl₂ and 4.6×10^{-7} for the sulfide from CdSO₄. Approaching the equilibrium from the left by pre-

¹ LINDER and PICTON: *J. Chem. Soc.*, **61**, 114 (1892).

² VAN BEMMELLEN: *Z. anorg. Chem.*, **23**, 337 (1900).

³ HABER: *Ber.*, **55B**, 1730 (1922); BÖHM and NICLASSEN: *Z. anorg. Chem.*, **132**, 1 (1924).

⁴ ALLEN, CRENSHAW, and MERWIN: *Am. J. Sci.*, [4] **34**, 362 (1912); cf. BAUBIGNY: *Compt. rend.*, **142**, 577 (1906).

⁵ STANEK: *Z. anorg. Chem.*, **17**, 117 (1898).

⁶ STULL: *J. Am. Chem. Soc.*, **23**, 512 (1901); BRUNI and PADOA: *Atti accad. Lincei*, [5] **14**, II, 525 (1905).

cipitation studies, the constant is $k = 1.6 \times 10^{-6}$.¹ The variation from a constant value is not due to the existence of two different modifications of cadmium sulfide, as Bruni assumes, but to variation in the size of the particles. The particles form more slowly, are larger, and hence are less soluble from a cadmium chloride solution than from a cadmium sulfate solution.

A gel of cadmium sulfide is also obtained by the action of sodium thiosulfate on a solution of cadmium salt at the boiling point;² by the electrolysis of a solution of $\text{Na}_2\text{S}_2\text{O}_3$ containing a little NaCl , with a cadmium anode and an indifferent cathode; and by the alternating current electrolysis of 10 per cent $\text{Na}_2\text{S}_2\text{O}_3$ solution with cadmium electrodes.³ A more satisfactory electrolytic method appears to be the electrolysis of a sodium sulfate solution with a cadmium anode and a cathode consisting of a mixture of copper sulfide and sulfur.⁴ The electrolytic methods have been suggested for the technical formation of cadmium yellow and will be referred to again in the chapter on pigments.

In general, the color of cadmium sulfide gel is light yellow when thrown down from cold solutions of low cadmium content by hydrogen sulfide or by alkali sulfides, whereas the color is a deep orange when precipitated from hot acid cadmium solutions with hydrogen sulfide or by boiling cadmium solutions with an excess of sodium thiosulfate. Microscopic crystals likewise vary in color from clear yellow to orange. The cause of the variation in color will be considered in detail in a subsequent chapter.⁵

Precipitated cadmium sulfide is always contaminated by anions in the solution from which it separates. The determination of cadmium as sulfide, especially in the presence of sufficient hydrochloric acid to ensure its separation from zinc, has long been regarded as a useless method because of the chloride carried down with the precipitate. Treadwell⁶ attributes the contamination to the formation of a double salt, $\text{CdS} \cdot \text{CdCl}_2$, in varying amounts depending on the acid concentration and the tempera-

¹ BRUNI and ZAWADSKI: *Bull. acad. Krakow.*, 296 (1909).

² DONATH: *Z. anal. Chem.*, **40**, 141 (1901).

³ RICHARDS: *Trans. Am. Electrochem. Soc.*, **1**, 221 (1902).

⁴ LORENZ: *Z. anorg. Chem.*, **12**, 442 (1896); BERNFELD: *Z. physik. Chem.*, **25**, 46 (1898).

⁵ P. 115.

⁶ TREADWELL-HALL: "Analytical Chemistry," **2**, 191 (1912).

ture and pressure at which the precipitation is carried out. Egerton and Raleigh¹ believe the precipitate to have a constant composition when thrown down at 80° from a solution containing 4 cubic centimeters of concentrated hydrochloric acid in 100 cubic centimeters, and washed with an unspecified, definite quantity of water. Under these conditions, the precipitate is said to contain 8.16 per cent of the alleged salt, $\text{CdS} \cdot \text{CdCl}_2$; hence, in determining cadmium quantitatively by weighing the sulfide, the molecular weight of the precipitate is taken to be 147.4 instead of 144.47 for pure cadmium sulfide.

Since conclusive evidence of the existence of a definite double salt $\text{CdS} \cdot \text{CdCl}_2$ is lacking, it is probable that the contamination of the sulfide gel is due to adsorption of cadmium chloride in varying amounts depending on the conditions. To test this hypothesis,² hydrogen sulfide at room temperature was passed into a definite volume of solution containing a constant amount of cadmium chloride and varying amounts of hydrochloric acid. The precipitate was filtered on a Gooch crucible, washed until the wash water gave no test for chloride and then analyzed for the chlorine content. The results are given in Table XVII and shown graphically by curve A of Fig. 9. The

TABLE XVII.—ADSORPTION OF CHLORIDE BY CADMIUM SULFIDE
PRECIPITATED AT 25° (FIG. 9, CURVE A)

Cubic centimeters $N/10 \text{ CdCl}_2$, total volume, 75 cubic centimeters	Final normality of HCl	Chlorine adsorbed, milligrams	$\frac{\text{Cl}}{\text{CdS}^1} \times 100$
25	0.033	3.61	2.00
25	0.068	4.67	2.59
25	0.121	6.44	3.51
25	0.156	7.64	4.23
25	0.209	8.15	4.51
25	0.349	9.47	5.24
25	0.419	9.96	5.52
25	0.507	9.45	5.23
25	0.596	9.23	5.11
25	0.664	6.74	3.73

¹ Corresponding to 25 cubic centimeters of $N/10 \text{ CdCl}_2$.

² J. Chem. Soc., 123, 3019 (1923).

WEISER and DURHAM: J. Phys. Chem., 32 (1928).

filtrates were tested for completeness of precipitation by rendering them alkaline with ammonia and saturating with hydrogen sulfide. With the most acid solution a faint yellow coloration was noted but no precipitate. The amount of cadmium required to produce this coloration was found to be negligible as compared with the total amount of precipitate.

An attempt was made to repeat the above observations at 80° as recommended by Egerton and Raleigh, but precipitation was

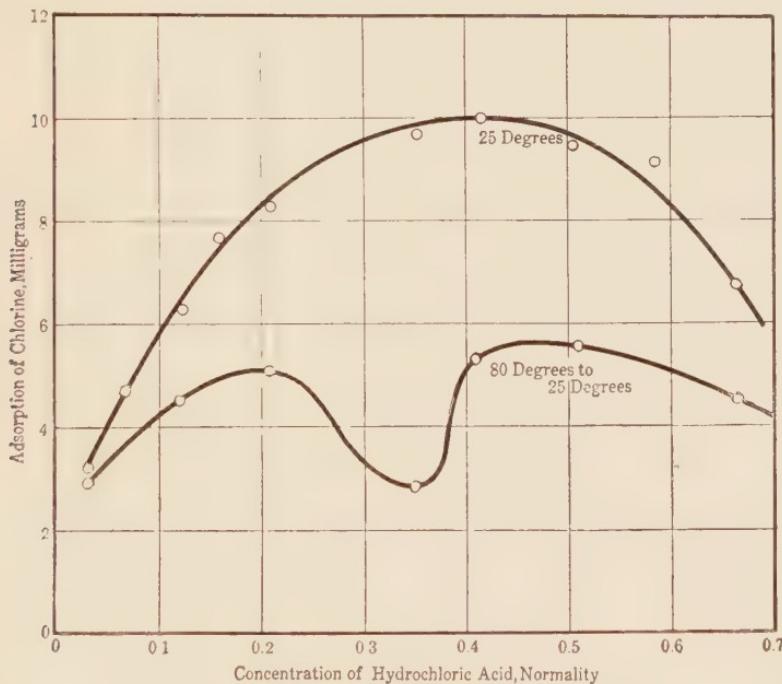


FIG. 9.—Adsorption of chlorine by cadmium sulfide.

found to be far from complete. Accordingly, the several solutions were heated to 80°, removed from the source of heat, and hydrogen sulfide conducted through continuously while they cooled down to room temperature. The precipitates were washed and analyzed for chloride with the results given in Table XVIII and shown graphically in curve *B* of Fig. 9.

Referring to curve *A*, it will be seen that the amount of chlorine in the precipitate does not increase continuously with the concentration of hydrochloric acid but exhibits a maximum. This

TABLE XVIII.—ADSORPTION OF CHLORIDE BY CADMIUM SULFIDE
PRECIPITATED BETWEEN 80 AND 25° (FIG. 9, CURVE B)

Cubic centimeters of N/10 CdCl ₂ , total volume, 75 cubic centimeters	Final normality of HCl	Chlorine adsorbed, milligrams	$\frac{\text{Cl}}{\text{CdS}^{\ddagger}} \times 100$
25	0.033	2.88	1.59
25	0.121	4.52	2.50
25	0.209	5.06	2.80
25	0.279	3.64	2.02
25	0.349	2.87	1.59
25	0.419	5.38	2.98
25	0.507	5.58	3.09
25	0.664	4.59	2.54

[†] Corresponding to 25 cubic centimeters of N/10 CdCl₂.

maximum is due to a visible change in the physical character of the precipitate from a flocculent to a distinctly granular structure. The curve is thus a typical adsorption curve showing a maximum due to a physical change in the adsorbent.¹

Curve B for the second series of experiments lies under curve A, as would be expected since the temperature at which the precipitation starts is higher, hence the precipitate is more granular and the adsorption is less. With increasing concentration of acid, the adsorption of chloride increases so that the first part of curve B is very similar to that of curve A, and for the same reason. But when the acid reaches a concentration in the neighborhood of 0.3 normal, the amount of cadmium sulfide precipitated in the hot decreases with a corresponding increase in the amount precipitated at lower temperatures. This means a larger amount of finely divided particles and a correspondingly greater adsorption which rises to a second maximum. This behavior would be difficult to explain on the basis of double salt formation but is readily accounted for by considering the contamination as a case of adsorption. The final concentration of acid recommended by Egerton and Raleigh was approximately 0.5 normal. This might appear to account for the constancy of composition of their precipitates since curve B is relatively flat when the hydro-

¹ Cf. p. 216.

chloric acid concentration is in the neighborhood of 0.5 normal. However, the chlorine content under these conditions corresponds to 12.2 per cent of the alleged double salt instead of to 16.5 per cent as calculated from Egerton and Raleigh's results. The difference is, of course, in the conditions of the precipitation.

CADMIUM SULFIDE SOLS

A sol of cadmium sulfide is best prepared by precipitating an ammoniacal solution of CdSO_4 or CdCl_2^1 with hydrogen sulfide, washing the precipitate by decantation, and suspending in water through which hydrogen sulfide is conducted until peptization is complete. The excess hydrogen sulfide can be removed by boiling.

A sol is obtained directly by conducting hydrogen sulfide into a solution of cadmium sulfate, provided the concentration is no stronger than 0.0002 molar.² Such a preparation is not very stable but the stability may be increased by the presence of casein, gum arabic,³ soaps,⁴ and probably by sugar, since the latter is adsorbed by the colloidal particles.⁵ If a solution of a cadmium salt is poured on a 5 per cent gelatin gel containing sodium sulfide, the cadmium ion diffuses into the gel precipitating a clear, golden yellow, transparent layer of sol.

The sol prepared by Prost's method is a beautiful golden yellow in transmitted light and is somewhat fluorescent in reflected light. Dilute sols are quite stable for a considerable time but a preparation containing as much as 11 grams per liter precipitates in 24 hours. The particles are negatively charged,⁶ the ratio of the precipitating power of the sulfates of potassium, aluminum, and cadmium being 1:140:150. The high precipitating power of cadmium salts is doubtless due to removal of the stabilizing electrolyte, hydrogen sulfide. Plant and animal fibers are

¹ PROST: *Bull. acad. roy. Belg.*, '3, **14**, 312 (1887); *J. Chem. Soc.*, **54**, 653 (1888).

² MÜDRUM: *Chem. News*, **79**, 170 (1899); VANINO and HARTL: *Ber.*, **37**, 3622 (1904).

³ MELLER and ARTMANN: *Oesterr. Chem. Ztg.*, **7**, 149 (1904).

⁴ BHATNAGAR, PRASAD, and BAHL: *Quart. J. Indian Chem. Soc.*, **2**, 11 (1925).

⁵ PRASAD, SHRIVASTAVA, and GUPTA: *Kolloid-Z.*, **37**, 101 (1925).

⁶ BILTZ: *Ber.*, **37**, 1101 (1904).

colored by colloidal cadmium sulfide;¹ but the color is not adsorbed sufficiently strongly to serve as a dye.

A benzine sol of cadmium sulfide may be prepared by triturating the gel with heavy oil and shaking the mixture with the light petroleum distillate.² Oleates may be used as protective colloids in the preparation of zinc and cadmium sulfide sols in benzene, toluene, benzine, and linseed oil.³

COLLOIDAL MERCURIC SULFIDE

A black mercuric sulfide gel is thrown down by the action of excess hydrogen sulfide on a mercuric salt in an acid or neutral solution. The tendency for the precipitated sulfide to form microcrystals increases with increasing atomic weight in the zinc-cadmium-mercury family, the gel of mercuric sulfide thrown down at 0° giving an x-radiogram characteristic of a crystalline structure.⁴ The black crystals possess the cubic structure similar to zinc blende and identical with the mineral metacinnabarite.

When mercuric chloride is precipitated with hydrogen sulfide or a soluble sulfide, the precipitate may be first white, then yellow, and finally black. The white precipitate is $2\text{HgS} \cdot \text{HgCl}_2$, the black is HgS , and the yellow is a mixture of the two.⁵ If an excess of sodium sulfide is added, a sol is formed which is yellow at first and then changes to black.⁶

Black mercuric sulfide is also obtained by the action of mercuric chloride on a solution of sodium thiosulfate at concentrations in which the ratio of HgCl_2 to $\text{Na}_2\text{S}_2\text{O}_3$ lies between 2:3 and 1:4. At higher thiosulfate concentrations red mercuric sulfide is precipitated.⁷ The black gel is formed by the alternating-current electrolysis of hot sodium thiosulfate solution with mercury electrodes.⁸ Since the alternating current causes the mercury to vibrate, the surface of the latter is kept free from precipitated

¹ BILTZ: *Chem. Zentr.*, I, 1039 (1904).

² VAN DORP and RODENBURG: *Chem. Weekblad*, 6, 1038 (1909).

³ BECHHOLD and SZIDON: *Kolloid-Z. (Zsigmondy Festschrift)* 36, 259 (1925).

⁴ BÖHM and NICLASSEN: *Z. anorg. Chem.*, 132, 1 (1924).

⁵ JOLIBOIS and BOUVIER: *Compt. rend.*, 170, 1497 (1920).

⁶ MOROSOW: *Kolloid-Z.*, 36, 21 (1925).

⁷ ALLEN, CRENSHAW, and MERWIN: *Am. J. Sci.*, [4] 34, 351 (1912).

⁸ WEISER: *J. Phys. Chem.*, 22, 77 (1918).

sulfide; hence, the current efficiency is much higher than obtains in the alternating-current electrolysis with zinc and cadmium electrodes under similar conditions. Moreover, the mercury electrodes are uniform and the experimental conditions are therefore reproducible. In Fig. 10 the current efficiency at

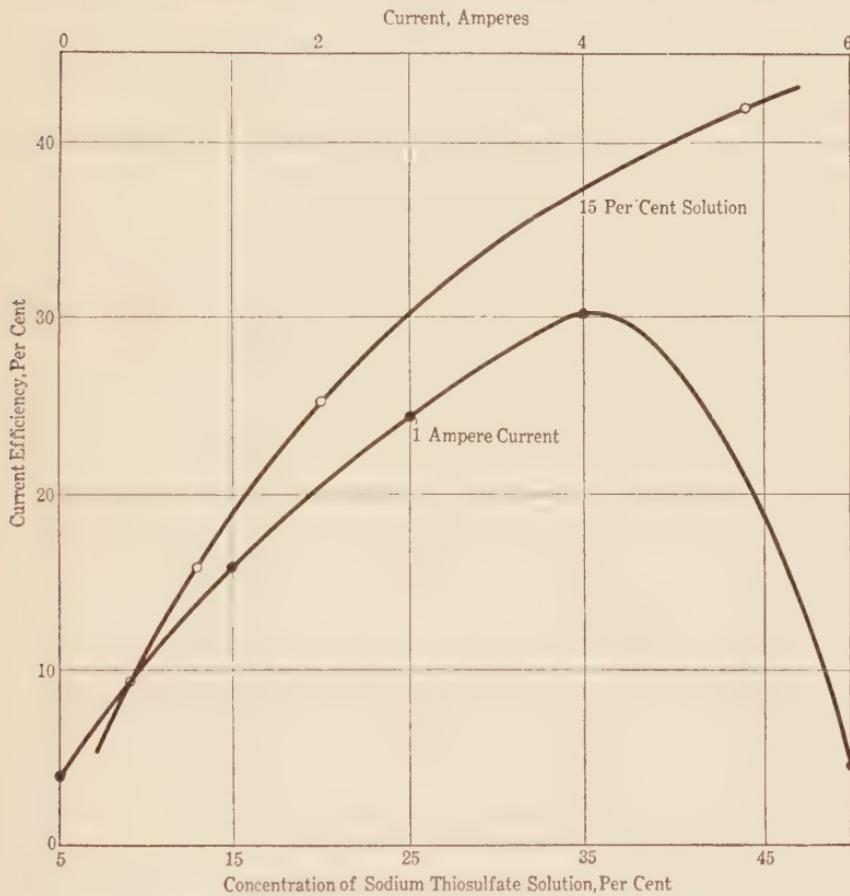


FIG. 10.—Efficiency of electrolysis of sodium thiosulfate solutions with mercury electrodes and a 60-cycle alternating current.

varying concentrations of electrolyte and at varying current densities is shown for a 60-cycle alternating current. The marked falling off in the efficiency with thiosulfate solutions stronger than 35 per cent is due to the rapid action of the hot electrolyte on the mercury, forming a film which prevents the rhythmical pulsations of the surface.

Red mercuric sulfide or cinnabar is the stable modification at all temperatures up to its sublimation point, about 580°. It is formed from the black gel by digesting the latter with alkali or ammonium sulfide. The process consists in the solution of the black regular form and the subsequent precipitation of the less soluble red hexagonal modification. The red sulfide precipitates directly when $\text{Hg}(\text{SH})\text{CNS}$ is boiled with concentrated NH_4CNS or when hydrogen sulfide is conducted into a warm mercuric salt solution in the presence of acetic acid and excess NH_4CNS or $\text{CS}(\text{NH}_2)_2$.¹ The interaction of mercuric chloride and concentrated sodium thiosulfate gives a red sulfide which Allen, Crenshaw, and Merwin took to be a third allotropic modification; but x-radiograms proved it to be identical with cinnabar.² When properly prepared, red mercuric sulfide furnishes a valuable red pigment known as vermillion.³

When zinc sulfide and manganese sulfide are precipitated together, a mixture is obtained from which manganese sulfide cannot be dissolved by acetic acid. A mixed precipitate of zinc sulfide and mercuric sulfide cannot be freed from mercury by digesting with sodium sulfide; conversely, mercuric sulfide precipitated from acid solution in the presence of zinc, contains about 3 per cent of zinc. Moreover, a cadmium solution so strongly acid that no precipitate is obtained with hydrogen sulfide will precipitate a great deal of the cadmium sulfide on adding a small amount of mercury solution. Feigl⁴ attributes this behavior to the formation of what he terms iso- or heteropolymers. While one cannot deny the possible existence of mixed salts such as $2\text{HgS} \cdot \text{MnS}$, it is probable that in many instances the contamination is due to adsorption.

MERCURIC SULFIDE SOLS

The sol of mercuric sulfide is easily prepared by washing the black loose gel with water and suspending in water through which

¹ VENKATARAMAIAH and RAO: *J. Sci. Assocn. Maharajah's College*, **1**, 41 (1923); *Chem. Abstr.*, **18**, 626 (1924); cf. ALVISI: *Atti accad. Lincei*, **7**, 97 (1898).

² KOLKMEIJER, BIJVOET, and KARSSEN: *Rec. trav. chim.*, **43**, 894 (1924).

³ See p. 118.

⁴ *Z. anal. Chem.*, **65**, 25 (1924).

a rapid current of hydrogen sulfide is passed.¹ If the gel has aged until it possesses a metallic appearance with a greyish tinge, peptization is accomplished with difficulty if at all. Excess hydrogen sulfide may be removed by boiling, but it is better to wash with hydrogen. The concentrated sol is deep black while the dilute sol is brown with a greenish fluorescence in reflected light.

A sol results on conducting hydrogen sulfide into a cold saturated solution of mercuric cyanide.² Owing to the low ionization of hydrocyanic acid, it has only a slight precipitating action; but the sol is more stable when the impurity is removed, preferably by distillation under reduced pressure in an atmosphere of hydrogen sulfide. An aerosol can be prepared in a similar way by conducting dry hydrogen sulfide into an alcoholic solution of mercuric cyanide³ and dialyzing against pure alcohol, using a membrane of parchment or collodion.⁴

The sodium salts of lysalbinic and protalbinic acids may be used as protective colloids in preparing a stable sol for medicinal purposes.⁵ When injected intravenously the sol is quite rapidly coagulated and becomes attached to the tissues. If the injection is subcutaneous, the sulfide remains in the subcutaneous tissue but if it is injected intravenously, the salt appears in the liver, spleen, bone marrow, and lungs from which it is absorbed slowly. Its administration is said to facilitate the healing of syphilitic lesions.⁶

Adsorption during Precipitation.—The adsorption of cations during the precipitation of negative mercuric sulfide is less than with the more hydrous arsenic trisulfide sol. Freundlich and Schucht⁷ determined the precipitation values for a number of salts and the adsorption of cations at the precipitation value in an attempt to show that equivalent amounts of all cations are

¹ WINSSINGER: *Bull. soc. chim.*, [2] **49**, 452 (1888); FREUNDLICH and SCHUCHT: *Z. physik. Chem.*, **85**, 641 (1913).

² LOTTERMOSER: *J. prakt. Chem.*, [2] **75**, 293 (1907).

³ ERRERA: *Kolloid-Z.*, **32**, 240 (1923).

⁴ OSTWALD and WALSKI: *Kolloid-Z.*, **28**, 228 (1921).

⁵ WOLVEKAMP: British Patent, 188772 (1921).

⁶ QUATTRINI: *Chem. Abstr.*, **10**, 640 (1916); SABBATANI: *Ibid.*, **11**, 1206 (1917).

⁷ Z. *physik. Chem.*, **85**, 641 (1913).

adsorbed at this concentration. Their observations are recorded in Table XIX. Since the adsorption values vary all the way from 0.004 to 0.050 milliequivalent per gram, the results would seem to disprove the assumption.¹ While the precipitation values of

TABLE XIX

Cation	Adsorption at precipitation value, milliequivalent	Precipitation value, millimols	Concentration of colloid, grams per liter
NH ₄	0.050	10.20	13.74
Ag.....	0.020	0.28	11.74
New magenta.....	0.008	0.097	13.74
Brilliant green.....	0.004	0.048	8.38
Auramine.....	0.011	0.094	10.05
Methylene blue.....	0.007	0.097	14.96
Ba.....	0.044	0.510	8.29
Cu [Cu(NO ₃) ₂].....	0.030	0.150	8.26
Cu (CuSO ₄).....	0.022	0.260	14.43
Ce.....	0.012	0.082	10.45

new magenta and methylene blue are identical and the adsorption values are almost the same, the precipitation value of auramine is but 3 per cent lower than that of new magenta; but the adsorption value is 37 per cent higher. Moreover, the precipitation value of brilliant green is only one-half that of new magenta and the adsorption value at this concentration is but half as much instead of being the same or larger in accord with Freundlich's conclusions from experiments on the adsorption of organic cations by arsenic trisulfide. There is no doubt that the anion has some effect but this cannot account for the precipitation value of CuSO₄ being 75 per cent higher than for Cu(NO₃)₂ and the adsorption of copper from nitrate solution being 25 per cent greater than from sulfate solution.

As in the case of arsenic trisulfide and the hydrous oxides, to which reference has been made² the variation from equivalent adsorption at the precipitation value is due to adsorption by the particles during agglomeration. This, however, seems inade-

¹ Cf. WEISER and MIDDLETON: *J. Phys. Chem.*, **24**, 30 (1920).

² Cf. p. 37.

quate to account for the much wider variation from equivalence with mercuric sulfide than with arsenic trisulfide. Fajans and Beckerath¹ point out that equivalent amounts of precipitating ions will produce the same discharging effect only so long as their distances from one another in the surface of the colloidal particle is sufficiently large; but this factor cannot account for the wide variation observed with ions of the same valence. The real cause of the variation is probably connected closely with the phenomenon to be considered in the next section.

Reversal of Adsorption.—When mercuric sulfide sol is first flocculated, the precipitate is highly gelatinous but it becomes granular quite rapidly and gives up a part of the adsorbed electrolyte. It is probable that the physical character of the precipitated sulfide varies appreciably with different electrolytes, thus accounting for the greater variation from equivalent adsorption by mercuric sulfide than by arsenic trisulfide.

The course of the adsorption reversal of mercuric sulfide has been followed by Freundlich.² Portions of 250 cubic centimeters each of a sol were treated with 25 cubic centimeters of auramine of varying concentrations. The mixtures were stirred continuously and at intervals samples were withdrawn, freed from suspended sulfide, and analyzed colorimetrically. The results of the observations with three different concentrations of auramine are given in Fig. 11. The curves are S-shaped, indicating that the adsorption reversal and, hence, the coarsening of the particles is an autocatalytic process. Furthermore, the velocity of the process rises rapidly with increasing concentration of the coagulating electrolyte. The mechanism is about as follows: When sufficient electrolyte is added to a sol, the charge on the colloidal particles is reduced below the critical value necessary for agglomeration. If the electrolyte concentration is near the precipitation value, the primary particles of the flocks still possess a slight charge which tends to keep them from coalescing. But with crystalline particles which are not very hydrous, like those of mercuric sulfide, the low residual charge is not sufficient to prevent a gradual coalescence and packing

¹ *Z. physik. Chem.*, **97**, 478 (1921).

² FREUNDLICH and SCHUCHT: *Z. physik. Chem.*, **85**, 660 (1913); FREUNDLICH and HASE: *Ibid.*, **89**, 417 (1915).

together of the particles thereby giving a diminished surface and a lessened adsorption. The rate of coalescence increases with diminishing residual charge and hence is greater the higher the

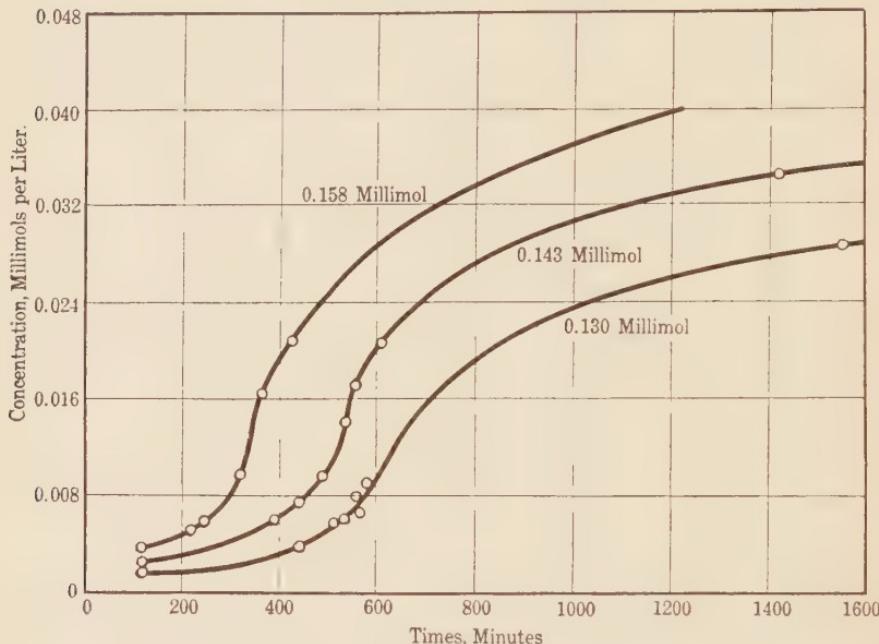


FIG. 11.—Velocity of the adsorption reversal after coagulation of mercuric sulfide sol with various concentrations of auramine.

concentration of precipitating electrolyte up to the point where charge reversal would come in. The apparent autocatalytic course may be the result of two processes: a slow initial formation of secondary aggregates from primary particles and a more rapid packing together of the larger aggregates.

CHAPTER VI

THE COLLOIDAL SULFIDES OF IRON, NICKEL, COBALT, MANGANESE, AND THE RARER ELEMENTS

COLLOIDAL SULFIDES OF THE IRON GROUP

Colloidal Ferrous Sulfide.—The black precipitate of ferrous sulfide thrown down from a cold ferrous salt solution with ammonium sulfide, is quite finely divided and may be peptized in part by thorough washing with cold water.¹ The sol is rather unstable, as is the one formed by passing hydrogen sulfide into a very dilute solution of a ferrous salt.² The stability is very much increased if the reaction is carried out in the presence of glycerin,³ gelatin, or sugar. Sabbatani⁴ investigated the pharmacological action of such sols when administered to dogs and rabbits. Since the particles were protected by an adsorbed film, the preparations were inactive so long as they remained colloidal.

Colloidal Nickel Sulfide.—It is well known that nickel sulfide is not precipitated by hydrogen sulfide in the presence of dilute hydrochloric acid and yet the precipitated sulfide obtained from alkaline solution is insoluble in dilute hydrochloric acid. Thiel and Ohl⁵ explain this behavior by postulating the existence of three isomeric forms of the sulfide: The α -sulfide is produced by mixing nickel salts slowly with dilute solutions of alkali sulfides at ordinary temperatures in the absence of air. It is readily soluble in the cold in mineral acids as dilute as 0.01 normal. In contact with water, its properties do not change very rapidly but in the presence of a solution which exerts a slight solvent action it goes over into the so-called β - and γ -forms. The β -sulfide is precipitated by hydrogen sulfide from a nickel

¹ BERZELIUS: "Lehrbuch der Chemie," 3rd ed., **3**, 439 (1834).

² WINSSINGER: *Bull. soc. chim.*, [2] **49**, 452 (1888).

³ MÜLLER and ARTMANN: *Oesterr. Chem. Ztg.*, **7**, 149 (1904).

⁴ *Atti accad. Lincei*, [5] **32**, II, 326, 473 (1923); **33**, I, 8; **33**, II, 228 (1924).

⁵ *Z. anorg. Chem.*, **61**, 396 (1909).

acetate solution acidified with acetic acid. It is insoluble in 2-normal hydrochloric acid in the cold but dissolves rapidly on boiling. The γ -sulfide results by boiling the β -form with acetic acid. It is probable that these three alleged isomeric forms of nickel sulfide are merely stages in the continuous transformation from the soluble to the insoluble state. There is no inversion point between any two of the alleged isomers and it is quite likely that any number of substances with intermediate properties could be formed. As is the case so frequently with the hydrous oxides, the very finely divided soluble and readily peptized particles of the newly formed precipitate go over gradually and continuously into larger and denser particles which are less soluble and less readily peptized. This change in physical character is always more rapid in contact with a medium which possesses a slight solvent action.

Unlike the sulfides of iron and cobalt, nickel sulfide has a marked tendency to form colloidal solutions, especially in the presence of an excess of ammonium sulfide. Every analyst is familiar with the dark brown coloration which forms gradually in a nickel salt solution to which ammonium sulfide is added. Many investigators have attributed this coloration to the formation of a sulfo-salt¹ as a result of the presence of an excess of sulfur in the ammonium sulfide reagent. This view was proven to be erroneous by Thiel and Ohl² who obtained the familiar brown-colored solution using ammonium sulfide entirely free from polysulfide. The latter investigators attributed the gradual development of the brown color to polymerization of nickel sulfide with the ultimate formation of a sol. As already indicated, it is more likely that the phenomenon is due to a gradual growth of the sulfide particles rather than to the formation of polymers. There is no doubt, however, that the color is due to nickel sulfide in colloidal solution. Thorne and Pates³ proved this conclusively when they ultrafiltered out the brown

¹ LECRENIER: *Chem. Ztg.*, **13**, 431, 449 (1889); DE KONINCK and LEDENT: *Z. angew. Chem.*, **5**, 203 (1891); DE KONINCK: *Compt. rend.*, **120**, 735 (1895); VILLIERS: *Ibid.*, **119**, 1208, 1263 (1894); ANTONY and MAGRI: *Gazz. chim. ital.*, **31**, II, 265 (1901).

² *Z. anorg. Chem.*, **61**, 396 (1909).

³ *Kolloid-Z.*, **38**, 155 (1926).

color completely from a sol prepared with the ordinary laboratory reagents.

An investigation of the factors influencing the formation of the brown sol was made by passing hydrogen sulfide directly into a nickel ammonium hydroxide solution, thereby avoiding the presence of any polysulfide. When the ammonia concentration is 100 grams per liter, a sol is formed with a nickel concentration between 2.0 and 0.01 grams per liter. Some precipitate forms on standing if the nickel concentration exceeds 1.0 gram per liter; below 0.01 gram per liter no coloration is observed. The range of nickel concentration between which a sol is formed, is determined by the ammonia concentration. For a sol containing 0.3 gram of the metal per liter, the ammonia concentration may be reduced to 45 grams per liter; for 0.2 gram nickel, 10 grams ammonia per liter; and for 0.1 gram nickel, 5 grams ammonia per liter. In every case, the sol must be kept saturated with hydrogen sulfide to prevent any precipitation. If the latter is removed completely, precipitation results but the precipitate is reprecipitated in part by adding more hydrogen sulfide even if the sulfide is allowed to age for several months. Moreover, the black residue obtained by taking the sol to dryness in a vacuum desiccator is partly reprecipitated by suspending in water and treating with ammonia and hydrogen sulfide.

The sol is quite stable in the absence of air. Boiling to remove hydrogen sulfide causes precipitation but the excess gas may be washed out with hydrogen or the excess ammonia removed in a vacuum desiccator without precipitation. The particles are negatively charged but alkali salts exert no precipitating action even in high concentration. Salts with multivalent cations cannot be used since they react either with the ammonia or the hydrogen sulfide.

Stable brown sols of nickel sulfide are not formed in the presence of an excess of ammonium polysulfide. Instead, a black precipitate is formed which cannot be washed without decomposition.¹ Analysis of an unwashed sample indicates a composition between NH_4NiS_4 and NH_4NiS_5 ; but the constitution is indefinite. It may be a sulfo-salt like the copper compound

¹ EPHRAIM: *Ber.*, **56B**, 1885 (1923).

NH_4CuS_4 ,¹ the ordinary nickel sulfide with adsorbed polysulfide, or a higher sulfide of nickel.

Villiers² developed a test for nickel which depends upon the formation of the brown sol. The nickel salt solution is treated with tartaric acid and a slight excess of sodium hydroxide. On passing in hydrogen sulfide, a part of the nickel sulfide is peptized, giving the characteristic dark brown color. Cobalt ions are precipitated as cobalt sulfide by this treatment except when a trace is present which is likewise peptized giving a brown sol.³ Tower showed that tartrate is essential for the stability of nickel sulfide sols prepared in alkali tartrate solution, complete precipitation resulting on removal of the organic ion by dialysis. A sol formed in the presence of glycerin⁴ is likewise thrown down by dialyzing out the organic stabilizing agent.

Colloidal Cobalt Sulfide.—The sol of cobalt sulfide may be prepared by the same procedures as are used to make colloidal nickel sulfide. As already noted, the tendency of the former to be peptized by ammonium sulfide is slight but a dilute sol is obtained by passing hydrogen sulfide into a cobalt solution containing an alkali tartrate. The only method so far described for preparing a stable sol involves the use of a protective colloid.

COLLOIDAL MANGANOUS SULFIDE

Ammonium sulfide and monosulfides of the alkali metals precipitate from a solution of a manganous salt, a rose or flesh-colored gel of manganous sulfide which oxidizes readily in the air, assuming a brown tint. The precipitation is very slow or incomplete from dilute solutions unless a salt such as ammonium chloride is present.⁵ It is probable that this salt acts by preventing sol formation. Citrates and tartrates prevent the precipitation of manganous sulfide by ammonium sulfide and citrates stop the precipitation by alkali sulfides as well.⁶ It is

¹ GLUUD: *Ber.*, **55B**, 952 (1922); GLUUD and MÜHLENZYCK: *Ibid.*, **56B**, 899 (1923).

² *Compt. rend.*, **119**, 1263 (1894); **120**, 46 (1895).

³ TOWER: *J. Am. Chem. Soc.*, **22**, 501 (1900); TOWER and COOKE: *J. Phys. Chem.*, **26**, 728 (1922).

⁴ MÜLLER and ARTMANN: *Oesterr. Chem. Ztg.*, **7**, 149 (1904).

⁵ JOULIN: *Ann. chim. phys.*, [4] **30**, 275 (1873).

⁶ HOW: *Chem. News*, **19**, 137 (1869).

altogether likely that these strongly adsorbed anions act by forming a stable negative sol.

The rose-colored sulfide appears to be the stable form when precipitated with alkali sulfides; but when thrown down with ammonium sulfides it frequently assumes a green color. Conditions favorable for the transformation have been given by a number of people.¹ The various methods have been analyzed critically by Mickwitz and Landesen² who reached the conclusion that the transformation never takes place except in the presence of free ammonia. If no free ammonia is present, the rose-colored sulfide precipitated by pure NH_4HS contains more sulfur than is required by the formula MnS and is better expressed by the formula $\text{H}_2\text{Mn}_3\text{S}_4$ or $3\text{MnS} \cdot \text{H}_2\text{S}$. In the presence of free ammonia, on the other hand, the composition may be expressed by the formula $\text{NH}_4\text{HMn}_3\text{S}_4$ or $3\text{MnS} \cdot \text{NH}_4\text{HS}$, and this rose-colored gel goes over slowly into the green form of MnS , giving up NH_4HS to the mother liquor.

While the presence of ammonia appears to be of primary importance for the spontaneous transformation of rose to green manganous sulfide, the mechanism of the action of the ammonia is by no means established. Nothing is proved by assuming the existence of compounds, one of which is stable and the other unstable. The alleged compounds $\text{H}_2\text{Mn}_3\text{S}_4$ and $\text{NH}_4\text{HMn}_3\text{S}_4$ are probably manganous sulfide gels with adsorbed H_2S and adsorbed NH_4HS , respectively. It is not clear, however, why the adsorption of hydrogen sulfide and alkali sulfides should stabilize the rose sulfide while adsorbed ammonium hydrosulfide does not. Obviously, this whole problem of the stability of the rose sulfide calls for further investigations. It is generally taken for granted that the rose and green sulfides are two isomeric forms; but this point has not been definitely established. It is recognized that the transformation from rose to green is accompanied by a change from an amorphous or microcrystalline state

¹ FRESENIUS: *J. prakt. Chem.*, **82**, 267 (1861); CLASSEN: *Z. anal. Chem.*, **8**, 370 (1869); **16**, 319 (1877); MEINEKE: *Z. angew. Chem.*, **1**, 4 (1888); OLSEN, CLOWES, and WEIDMANN: *Chem. Zentr.*, I, 468 (1905); SEELIGMANN: *Z. anal. Chem.*, **53**, 594 (1914); **54**, 104 (1915); FISCHER: *J. Russ. Phys. Chem. Soc.*, **46**, 1481 (1914); VILLIERS: *Compt. rend.*, **159**, 67 (1914); HAHN: *Z. anorg. Chem.*, **121**, 209 (1922).

² *Z. anorg. Chem.*, **131**, 101 (1923).

to a denser and definitely crystalline form. An x-ray examination of the two preparations would probably show whether the color change is due to a change in physical character or in molecular structure.

A red or orange manganese sulfide is said to precipitate from a weakly acid solution of a manganese salt by the prolonged action of hydrogen sulfide.¹ Olsen and Rapalje² claim that the ordinary flesh-colored sulfide is a mixture of the red sulfide with a gray form.

COLLOIDAL SULFIDES OF INDIUM AND THALLIUM

Colloidal Indium Trisulfide.—Yellow indium trisulfide is precipitated by conducting hydrogen sulfide into a solution of an indium salt which is not too acid nor too concentrated.³ If the hydrous oxide of indium, $In_2O_3 \cdot xH_2O$, is suspended in water through which hydrogen sulfide is passed, a golden-yellow negative sol of the sulfide is produced.⁴ This sol may be boiled to remove excess hydrogen sulfide without flocculation but it is quite unstable in the presence of electrolytes, especially those with strongly adsorbed cations.

Colloidal Thallous Sulfide.—Thallous sulfide, Tl_2S , is precipitated in a finely divided hydrous condition when hydrogen sulfide or ammonium sulfide is added to an alkaline or acetic acid solution of a thallous salt. Incomplete precipitation of the hydrous sulfide results, also, when sodium hyposulfite is added to a thallous salt solution. When formed in this way the mass is reddish brown at first, then violet, and finally black.⁵ If the cold solution from which the salt separates contains a trace of free sulfuric acid, it come down as microscopic tetrahedra.⁶ The sol of thallous sulfide is prepared by passing hydrogen sulfide into a very dilute solution of a thallous salt and dialyzing the product.⁷

¹ VÖLKEL: *Liebig's Ann.*, **59**, 27 (1846); FISCHER: *J. Russ. Phys. Chem. Soc.*, **46**, 1481 (1914).

² *J. Am. Chem. Soc.*, **26**, 1615 (1904).

³ WINKLER: *J. prakt. Chem.*, **94**, 1 (1865); **102**, 273 (1867).

⁴ LINDER and PICTON: *J. Chem. Soc.*, **61**, 134 (1892).

⁵ BRUNCK: *Liebig's Ann.*, **336**, 281 (1904).

⁶ HEBBERLING: *Liebig's Ann.*, **134**, 11 (1865).

⁷ WINSSINGER: *Bull. soc. chim.*, [2] **49**, 452 (1888).

Thallie sulfide, Tl_2S_3 , is not precipitated by the action of hydrogen sulfide on an aqueous solution of a thallie salt for, if formed at all, it is reduced instantly to thallous sulfide and free sulfur.¹

COLLOIDAL SULFIDES OF GERMANIUM

Germanium Monosulfide.—Germanium monosulfide,² GeS , is precipitated as a reddish-brown hydrous mass when hydrogen sulfide is passed into a hydrochloric acid solution of germanous oxide. The freshly formed precipitate is readily peptized by washing, giving an orange-red to brown sol, which is quite stable if kept out of contact with air. The sol is negatively charged and is readily flocculated by acids and by salts with multivalent cations.

Germanium Disulfide.—Germanium disulfide, GeS_2 , is thrown down by hydrogen sulfide from strongly acid solutions of germanium dioxide. An aqueous solution of the dioxide gives no precipitate with hydrogen sulfide and the precipitation is incomplete from a slightly acidified solution. The sulfide comes down as a white luminous gel which is peptized by washing, giving an opalescent negative sol. The salt decomposes slightly in contact with water, yielding hydrogen sulfide. Hence, when the sol is flocculated by heavy metal salts the coagulum has the color of the heavy metal sulfides.

COLLOIDAL SULFIDES OF MOLYBDENUM AND TUNGSTEN

Colloidal Molybdenum Sulfide.—The trisulfide of molybdenum, MoS_3 , is precipitated when hydrogen sulfide is passed into a concentrated solution of a molybdate followed by the addition of hydrochloric acid. It is also formed by boiling the molybdate of an alkali metal for a short time with ammonium sulfide and then precipitating with dilute mineral acid. Winssinger³ prepared the sol by adding to a dilute solution of potassium sulfomolybdate slightly more than enough acid to liberate the sulfide, and dialyzing. The transparent brown sol was quite stable; but if the preparation was not purified by dialysis it coagulated in a few hours.

¹ STRECKER: *Liebig's Ann.*, **135**, 207 (1865).

² WINKLER: *J. prakt. Chem.*, [2] **34**, 177 (1886); **36**, 177 (1887).

³ *Bull. soc. chim.*, [2] **49**, 452 (1888).

Hydrous molybdenum pentasulfide is precipitated as a brownish-black mass by reducing with zinc an ammonium molybdate solution containing 20 per cent sulfuric acid, and passing in hydrogen sulfide.¹ A sol of this sulfide has not been described.

Svedberg² prepared a sol of molybdenum disulfide in isobutyl alcohol by passing an oscillating discharge between electrodes of molybdenite. In a similar way von Hahn³ prepared a blue hydrosol. A sol was also formed by cathodic disintegration of the molybdenum mineral.⁴

Tungsten Trisulfide.—The trisulfide of tungsten, WS_3 , is precipitated by adding acid to a solution of tungsten trioxide in ammonium sulfide or by saturating an aqueous solution of a tungstate with hydrogen sulfide and acidifying. The precipitate is much more finely divided than the corresponding molybdenum salt and runs through the filter during washing. If the washed sulfide is suspended in boiling water, it is largely peptized, forming a brown sol.⁵ Winssinger⁶ prepared the sol by adding slightly more acid to a sodium thiotungstate solution than is necessary to free the sulfide. The color of the sol changes from a bright orange-red to a dark brown without agglomerating.

COLLOIDAL SULFIDES OF SELENIUM AND TELLURIUM

Colloidal Selenium Disulfide.—Several substances have been described as compounds of selenium and sulfur but they have all proved to be mixtures of the two elements⁷ which are known to form several series of mixed crystals.⁸ It is possible, however, that the sol formed by conducting hydrogen sulfide into an aqueous solution of selenium dioxide⁹ may contain some selenium

¹ KRÜSS: *Liebig's Ann.*, **225**, 1 (1884); MAWRROW and NOKOLOW: *Z. anorg. Chem.*, **95**, 188 (1916).

² "Die Methoden zur Herstellung kolloider Lösungen," 490 (1909).

³ *Kolloid-Z. (Zsigmondy Festschrift)* **36**, 277 (1925).

⁴ MÜLLER and LUCAS: *Z. Elektrochem.*, **11**, 521 (1905); LE BLANC: *Ibid.*, **11**, 813 (1905); Cf. p. 13.

⁵ BERZELIUS: "Lehrbuch der Chemie," 3rd ed., **3**, 126 (1834).

⁶ *Bull. soc. chim.*, [2] **49**, 452 (1888).

⁷ DIVERS and SHIMIDZU: *Chem. News*, **51**, 199 (1885).

⁸ RINGER: *Z. anorg. Chem.*, **32**, 183 (1902); RETGERS: *Z. physik. Chem.*, **12**, 583 (1893).

⁹ GUTHIER: *Z. anorg. Chem.*, **32**, 292 (1902); GUTBIER and LOHMANN: **42**, 325 (1904); **43**, 384 (1905).

sulfide. In any event, the preparation is always referred to as colloidal selenium sulfide. The sol possesses a bright yellow color in reflected light and red in transmitted light. It is very stable even in the presence of electrolytes but by adding hydrochloric acid and boiling or by exposure to light, a plastic red gel is precipitated.¹ Since selenium sol is red, it is possible that the red color of the coagulum is due to colloidal selenium dispersed in plastic sulfur. It should be possible to settle this point by an ultramicroscopic examination of the gel.

Colloidal Tellurium Sulfides.—Both tellurium disulfide, TeS_2 , and tellurium trisulfide, TeS_3 , are said to exist in the sol state when prepared and kept at low temperatures.² The disulfide sol is obtained by passing hydrogen sulfide into a cold solution of a tetravalent tellurium salt. During the gradual formation of the sulfide, the sol changes in color from yellow, orange, and reddish-brown to black with a bluish opalescence. If the reagents are pure the sol is quite stable. It is precipitated by freezing as reddish-brown flocks which are repeatized again after thawing.

The sol of tellurium trisulfide is formed by passing hydrogen sulfide into a cold dilute solution of telluric acid. The dialyzed preparation appears perfectly clear in transmitted light with a light blue to gray-violet color; but in reflected light it is cloudy and gray in color. Like the disulfide sol, it is quite stable and possesses similar properties. The similarity in behavior between the two sols indicates that both are primarily mixtures of colloidal tellurium and colloidal sulfur.

THE COLLOIDAL SULFIDES OF THE PLATINUM FAMILY

Of the sulfides of the platinum family of elements PdS , OsS_4 , Ir_2S_3 , and PtS_2 are known to form colloidal solutions. The sols of palladium monosulfide, osmium tetrasulfide, and platinum disulfide are formed by conducting hydrogen sulfide into dilute solutions of palladous chloride, osmium tetroxide, and platinic chloride, respectively.³ Of these sols, platinum disulfide is the most readily formed and the most stable. Indeed, the tendency of the salt to go into the colloidal state is so great that electrolytes

¹ VON HAHN: *Kolloid-Z.*, **27**, 172 (1920).

² GUTBIER: *Z. anorg. Chem.*, **32**, 292 (1902).

³ WINSSINGER: *Bull. soc. chim.*, [2] **49**, 452 (1888).

such as magnesium chloride must be added to the solution before conducting in hydrogen sulfide in the estimation of platinum as sulfide.¹ Freshly formed iridium sesquisulfide thrown down from a solution of the oxide by hydrogen sulfide is carried into colloidal solution by thorough washing.²

¹ IVANOV: *J. Russ. Phys. Chem. Soc.*, **48**, 527 (1916); GAZE: *Chem. Zentr.*, I, 464 (1913).

² BERZELIUS: "Lehrbuch der Chemie," 3rd ed., **3**, 222 (1834).

CHAPTER VII

PIGMENTS

Ordinary paints consist of three essential parts, the pigment, the medium or vehicle, and the drier or siccative. Pigments are finely divided insoluble colored powders. When mixed with suitable media they form paints. For oil paints, the media are usually vegetable drying oils of which linseed oil is by far the most important and most commonly used. For water-color paints, the vehicle consists of such substances as honey, glycerin, dextrin, and aqueous sols of the gums. The driers are oxygen carriers which catalyze the oxidation of the oil. Among the most important driers are suitable compounds of metals such as lead, manganese, and cobalt which have more than one valence. Certain pigments, notably litharge and white lead, possess the necessary siccative properties and a special drier is not required.

An ideal pigment should be quite stable chemically and should not react with any material with which it is likely to come in contact, either in the vehicle or on the surface which it covers. Actually, few pigments fulfill these ideal requirements, for few substances are capable of standing the action of light and the atmosphere, pure and impure, for indefinite periods of time. While it is obvious that no pigment is absolutely proof against destruction, it is equally true that all pigments are quite durable under certain conditions. The chemical characteristics which a pigment must possess are determined, therefore, by the conditions to which it will be subjected. In general, the most valuable pigments are to be found among the metallic oxides and the metallic salts of strong acids.

In addition to the chemical requirements, a pigment must possess the desired color, covering power, and hiding power. Since the physical state of the pigment, including the particle size, has such a profound effect on the above characteristics, one must approach this subject from the standpoint of colloid chemis-

try. The general principles involved are well illustrated by the colloidal sulfides.

ARSENIC SULFIDE PIGMENTS

Arsenic Trisulfide.—This sulfide known as King's yellow is a brilliant but fugitive and extremely poisonous pigment which was extensively used before the introduction of lead and barium chromate which are quite similar to it in color. The pigment is prepared by precipitation from an arsenious acid solution with hydrogen sulfide or by subliming a mixture of arsenic trioxide and sulfur. The sulfide is found native as the mineral orpiment which is sometimes ground up and used as a pigment.

Arsenic Disulfide.—This pigment occurs in nature as the mineral realgar. The commercial red arsenic glass or ruby sulfur is an artificial disulfide prepared by mixing arsenical pyrites and common pyrites in such proportion that the mixture contains about 15 per cent of arsenic and 27 per cent of sulfur. Such a mixture is then sublimed and the resulting product is melted with sulfur to give it the proper color. This so-called ruby sulfur is a red glassy mass consisting of arsenic disulfide and sulfur in varying amounts.¹ It was formerly used as an orange pigment but, like the trisulfide, it is no longer employed to any extent.

ANTIMONY SULFIDE PIGMENTS

Antimony Trisulfide.—Antimony trisulfides are usually divided into two classes; the natural varieties and the artificially prepared varieties. The first class includes black crystalline stibnite and a brick-red trisulfide called meta-stibnite which is said to be amorphous;² and the second class includes the colored sulfides which are sometimes used as pigments. The precipitated trisulfides have been classified into two sub-groups, those thrown down in the presence of hydrogen sulfide, and those thrown down in the absence of hydrogen sulfide. The first group includes the trisulfides precipitated by hydrogen sulfide direct and by the action of acids on the antimonates and thioantimonates. The color is usually some shade of orange and the group may be designated as the "antimony oranges." The pigments

¹ ROSCOE and SCHORLEMMER: "Treatise on Chemistry," 1, 708 (1920).

² BECKER: *Am. Phil. Soc.*, 25, 168 (1888).

are sometimes called the "antimony goldens" but the former term is preferable since antimony pentasulfide is called the golden sulfide of antimony. The second group of trisulfides are formed by the interaction of an antimonous salt and sodium thiosulfate.¹ The color is usually some shade of red and the group may be designated the "antimony crimsons."

Currie² has made an extended study of the factors influencing the color of antimony sulfide pigments. The interaction of dilute solutions of sodium thiosulfate and antimony trichloride at room temperature gives a light yellow precipitate which yields a fine yellow powder when washed and dried in vacuum. On heating at 100 to 110° in a hot-air oven, the color changes steadily through various shades of orange to a uniform red and finally to a rich crimson. Raising the temperature to 150 to 170° causes the color to change through a series of crimson shades to maroon, finally becoming uniformly black. The presence of salts, chlorides especially, and of acids, lowers the temperature at which the change to the black modification is complete.³

The wide variation in color from yellow through orange, crimson, and maroon to black is due entirely to variation in the size of the particles, the larger particles possessing the darker shades. Since sulfides tend to form negatively charged sols, the pigments formed in the presence of readily adsorbed anions are more highly peptized and hence are lighter in color than those precipitated in the presence of strongly adsorbed cations which favor coagulation into denser aggregates possessing a darker color. Moreover, the particles precipitated in the presence of gelatin are smaller and lighter in color than those obtained under similar conditions in the absence of a protective colloid.

The yellow and crimson trisulfides are amorphous as shown by x-radiograms but the final black product has a crystalline structure identical with the natural stibnite. The maroon shades are intimate mixtures of crimson with black sulfide. Various maroons can be synthesized by mixing the black and crimson powders. The densities of the sulfides change in exactly the same order as do the colors; the yellow pigments have a density

¹ Cf. LONG: *J. Am. Chem. Soc.*, **18**, 342 (1896).

² J. Phys. Chem., **30**, 223 (1926).

³ DE BACHO: *Ann. chim. applicata*, **12**, 143 (1919).

of approximately 4.10 to 4.12, the crimson 4.12 to 4.38, and the black 4.6 to 4.8.¹ The density of the maroon shades is usually about 4.4. to 4.5; the approximate density may be calculated by comparing the color of the maroon pigment with a mixture of known amounts of crimson and black sulfides of known density.

Stibnite and the artificial black sulfides are formed under conditions which would give relatively large crystals. Currie disintegrated stibnite in an electric arc under water according to Svedberg's method, obtaining a sludge of finely divided yellow crystalline particles. The fact that the crystalline sulfide may be either yellow or black, depending on the size of the particles, supports Berthelot's² contention that the transformation from one color to another involves no measureable heat effect. Currie was unable to prepare a crystalline crimson pigment, the larger particles of amorphous trisulfide alone giving the crimson color. It is possible, however, that the natural red meta-stibnite which is said to be amorphous would prove to be crystalline if examined with the x-rays.

Turning to the antimony oranges: The trisulfides, as ordinarily precipitated by hydrogen sulfide from a solution of trivalent antimony, are light golden yellow and may be dried in vacuum to give a rich golden color. Unlike the "antimony crimsons," heating to 105 to 110° causes little or no change in color while further heating to 150 to 170° causes the pigment to change through varying shades of brown to the black modification without showing any signs of the crimson color. The brown colors were found to be mixtures of amorphous golden with crystalline black trisulfide in varying proportions. Darkening through the crimson and maroon shades is prevented by adsorption of hydrogen sulfide on the surface of the golden particles which prevents them from coming into intimate contact and coalescing to the darker shades before the transformation to the black crystals takes place.

Both the orange and crimson trisulfide possess good hiding power and mix well with oil. They cannot, of course, be

¹ CURRIE: *J. Phys. Chem.*, **30**, 232 (1926); cf. KIRCHHOFF: *Z. anorg. Chem.*, **114**, 266 (1920); GUINCHANT and CHRÉTIEN: *Compt. rend.*, **138**, 1269; **139**, 51, 288 (1904); **142**, 709 (1906); ZANI: *Bull. acad. roy. méd. Belg.*, 1169 (1909).

² *Compt. rend.*, **139**, 97 (1904); cf., however, GUINCHANT and CHRÉTIEN: *ibid.*, **139**, 51 (1904).

employed with alkaline vehicles but they are quite stable in light and in the air. Crimson antimony is the most valuable red pigment employed in coloring rubber.¹

Antimony Pentasulfide and Tetrasulfide.—Antimony pentasulfide is frequently called the golden sulfide of antimony. Attention has been called² to the fact that the golden sulfide as usually prepared is a solid solution of tetrasulfide and sulfur. In general, the influence of temperature in the neighborhood of 100° on the golden sulfide is slight, a uniform darkening being the most noticeable effect. Above 115°, however, the tetrasulfide decomposes rapidly to trisulfide and sulfur, further heating producing color changes like those of all trisulfides precipitated in the presence of hydrogen sulfide.

Golden sulfide of antimony is a valued pigment for rubber goods and a number of recent patents have been granted for its commercial production.³ In the rubber industry the term "golden sulfide" is applied to a fairly wide range of products varying in shade from a golden yellow to a deep orange and in composition from a nearly pure antimony trisulfide to a mixture containing a relatively high percentage of tetrasulfide.⁴ In addition to its value as a pigment, antimony sulfide is superior to iron oxide pigment as a compounding ingredient. Mixes⁵ in which antimony sulfide is used, possess strength superior to similar mixes containing iron oxide. Moreover, mixes containing antimony sulfide possess good ageing qualities, whereas those containing iron oxide do not age well.⁶

CADMIUM SULFIDE PIGMENTS

Cadmium sulfide is much used by artists because of the brilliance of its color and its permanence. The yellow sulfide

¹ Cf. BIERER: *Chem. Age*, **28**, 194 (1920).

² See p. 62.

³ E.g., CHAILLAUX: British Patent, 151422 (1919); STARK: U. S. Patents, 1414836, 1415127 (1922); BEZZENBERGER: U. S. Patent, 1528394 (1925); WILSON: Canada Patent, 252563 (1925).

⁴ Cf. LUFT and PORRITT: *J. Soc. Chem. Ind.*, **40**, 275 T (1921).

⁵ The term "mixing" is applied to the operation by which sulfur and other materials are incorporated with rubber.

⁶ ANDERSON and AMES: *J. Soc. Chem. Ind.*, **42**, 136 T (1923); WOODWARD: *Rubber Age*, **1**, 99 (1917).

called "cadmium yellow" is obtained by precipitating cold solutions of low cadmium content with hydrogen sulfide or by precipitating cadmium solutions with the alkali sulfides. The deep orange pigment known as "cadmium orange" is precipitated from hot strongly acid solutions with hydrogm sulfide or by long boiling of cadmium solutions with sodium thiosulfate or alkali sulfide. Richards and Roopper¹ have patented processes for preparing cadmium yellow by electrolysis of a sodium thiosulfate solution with a cadmium anode and an indifferent cathode and by alternating-current electrolysis of thiosulfate solution with cadmium electrodes. The latter process is too inefficient to be of value² and the former has been improved by Fischer³ who substituted for the indifferent cathode one consisting of a mixture of equal parts of sulfur and copper sulfide, which has a relatively low resistance. The current efficiency of Fischer's process is 100 per cent. At a current density of 0.05 ampere per square centimeter, both yellow and orange sulfide are formed while at 0.005 ampere per square decimeter, only the yellow is obtained.

All the precipitated pigments are quite finely divided and have a high covering power. Since the electrolytic products are doubtless more expensive and are no better than those obtained by direct precipitation, there would appear to be no immediate future for the electrolytic processes.

The variation in color of the pigment was attributed to adsorbed impurities by Follenius⁴ and to the existence of allotropic modifications of different density and crystal structure by Buchner⁵ and by Klobukow.⁶ Thus, the latter found the specific gravity of the yellow preparations to vary from 3.906 to 4.143 and of the orange, from 4.47 to 4.513. Allen, Crenshaw, and Merwin⁷ showed, however, that there is but one crystalline form of the sulfide. The observed variations in density of the various

¹ RICHARDS: *Trans. Am. Electrochem. Soc.*, **1**, 221 (1902).

² WHITE: *Trans. Am. Electrochem. Soc.*, **9**, 305 (1906).

³ Z. *Elektrochem.*, **31**, 285 (1925); LORENZ: Z. *anorg. Chem.*, **12**, 442 (1896).

⁴ Z. *anal. Chem.*, **13**, 417 (1874).

⁵ Chem. Ztg., **11**, 1087, 1107 (1887).

⁶ J. *prakt. Chem.*, [2] **39**, 414 (1889).

⁷ Am. J. Sci., [4] **34**, 341 (1912); cf., however, EGERTON and RALEIGH. J. *Chem. Soc.*, **123**, 3019 (1923).

preparations are due to size of particles, the amount of adsorbed impurities, and the errors involved in determining the specific gravity of a mass composed of extremely minute particles. The variations in color are due to the size and physical character of the particles.

The amorphous or submicroscopically crystalline¹ powders vary from citron yellow to deep orange with increasing particle size. To illustrate: 4 grams of NaCl, 10 grams of Na₂S₂O₃, and 2 grams of CdSO₄ were added to 200 cubic centimeters of water and the solution kept boiling for some hours. The particles of the lemon-yellow precipitate obtained after 1 hour were too small to measure but after 5 hours, particles as large as 0.05 millimeter in diameter were formed and the pigment was bright orange in color.

Distinctly crystalline cadmium sulfides vary in color from clear yellow in tufts of hair-like needles to brownish yellow in the larger ones; but the powdered crystals are always orange. Thus, the light yellow gel formed by the action of an ammoniacal sulfide on a cadmium salt retains the same color after it has been digested until crystals identical with natural greenockite are produced; and the crystals become orange colored when powdered. This might seem to contradict the conclusion that the most finely divided particles of salt are yellow. It must be borne in mind, however, that in the last analysis the actual color is determined by the relative amounts of light transmitted and reflected.² Thus greenockite absorbs all the blue and part of the green of the spectrum and transmits the remainder. When the grains are in masses having diameters of 0.2 and 1.0 millimeter and are bounded by bright faces, a large amount of blue light is reflected directly by resonance and small amounts of red, orange, yellow, and green are reflected after passing through the surface layer of the crystals. The combined effect of all the reflected light is a lustrous dark yellow to yellowish green. Similarly, plane-faced bright crystals having diameters of but 0.01 millimeter or less, reflect about the same amount of blue by resonance but they reflect much more of the light which penetrates the surface, the resulting color being a pure yellow. A

¹ BÖHM and NICLASSEN: *Z. anorg. Chem.*, **132**, 1 (1924).

² ALLEN, CRENSHAW, and MERWIN: *Am. J. Sci.*, [4] **34**, 341 (1912).

mass of crystals of the same size with dull faces have a light yellow-brown color. The grains of powdered crystals usually have bright but not plane surfaces and give a brilliant orange color, for there is less direct reflection and much of the light finally reflected from the interior has penetrated deeper and thus lost more green and yellow than a powder having plane-faced fragments.

With the extremely minute sub-microscopically crystalline or amorphous particles, there is more absorption in the yellow and green and by transmitted light, the color appears orange yellow in films 0.01 millimeter thick. A powder with grains 0.0001 to 0.001 millimeter in diameter is bright yellow with a tinge of orange, and one with grains 0.004 to 0.007 millimeter in diameter, or compact aggregates of smaller granules, is bright orange.

VERMILION

Vermilion is the synthetic red hexagonal modification of mercuric sulfide which corresponds to the mineral cinnabar. The native product does not make a satisfactory pigment, for the impurities dull the color and it does not possess the desired physical character. The pigment is synthesized by dry and wet processes. The former, which is used most frequently, consists essentially in the formation of the black sulfide by direct union of mercury and sulfur, and its subsequent conversion into the red variety by a process of sublimation. Two dry processes are generally recognized: the Dutch process and the Chinese process.¹ The product prepared by the Chinese process is celebrated for its fine color which inclines to a carmine. At one time it was thought that the Chinese employed a wet method but this was not the case.² The Dutch and Chinese processes are essentially the same, any differences in physical character or color being due to the care exercised in the sublimation process.

The wet process depends on the fact that alkali and ammonium sulfides and polysulfides dissolve the black sulfide which subsequently precipitates as the less soluble red form.³ Rise in

¹ HURST and HEATON: "A Manual of Painters' Colors, Oils, and Varnishes," 5th ed., 163 (1913).

² *Chem. News*, **50**, 77 (1884); *J. Soc. Chem. Ind.*, **1**, 95 (1882).

³ BRUNNER: *Pogg. Ann.*, **15**, 593 (1829); FIRMENICH: *Dinglers polytech. J.*, **172**, 370 (1864).

temperature and excess sulfur favor the process.¹ The most satisfactory method of preparation is to heat the black sulfide at 100° in a closed vessel.² The black modification is more readily soluble in concentrated sodium or potassium sulfide than in ammonium sulfide. The pigment formed with alkali sulfide in the presence of excess mercuric salt is much darker than the vermillion powder formed with ammonium sulfide. The dark product consists of crystals sufficiently large to be easily recognized by the naked eye. When the larger crystals are ground up fine, the color is scarcely distinguishable from the ammonium sulfide preparation.

It is difficult to remove completely the adsorbed sulfide and sulfur from vermillion prepared in the wet way and these impurities are detrimental to the product. For this reason, Picton and Linder³ recommend heating the sol in a closed vessel from 160 to 170° for several hours until the desired shade of red is produced. Instead of starting with the black sulfide, Liebig⁴ heated freshly prepared infusible white precipitate, NH_2HgCl , with ammonium polysulfide at 45°; and Hausmann⁵ heated a solution of the white precipitate in concentrated sodium thiosulfate.

In addition to its use as a pigment in paint, vermillion is employed in making Chinese red ink and for coloring porcelain, paper, candles, etc. Most of the numerous temples throughout China are painted red with vermillion, since the Chinese look upon this as a lucky color.

MOSAIC GOLD

Mosaic gold is the name given to the pigment stannic sulfide which was extensively used in the eighteenth century as a golden coloring matter in paints. It was prepared then, as now, by subliming a mixture of tin amalgam, sulfur, and ammonium chloride. For example, on heating 18 parts of tin amalgam containing six parts of mercury with six parts of ammonium chloride and seven parts of sulfur, ammonium chloride, mercuric

¹ STANEK: *Z. anorg. Chem.*, **17**, 117 (1898); CHRISTY: *Am. J. Sci.*, [3] **17**, 453 (1879); IPPEN: *Z. Kryst.*, **27**, 110 (1897).

² ALLEN, CRENSHAW, and MERWIN: *Am. J. Sci.*, [4] **34**, 367 (1912).

³ British Patent, 5120 (1892).

⁴ Liebig's *Ann.*, **5**, 239; **7**, 49 (1833).

⁵ *Ber.*, **7**, 1747 (1874).

chloride, and stannous chloride sublime, leaving the pigment stannic sulfide in the form of beautiful golden yellow translucent scales.¹ At the present time it is employed as a bronzing powder for wood, metals, wallpaper, and gypsum plaster.

The zinc sulfide-barium sulfate pigment known as lithopone will be considered in the next chapter.

¹ WOULFE: *Phil. Trans.*, **61**, 114 (1771).

CHAPTER VIII

LITHOPONE

Lithopone is a white pigment consisting of an intimate mixture of barium sulfate and zinc sulfide prepared in a special way. The process patented in 1874 by John B. Orr consists in the double decomposition of barium sulfide and zinc sulfate in solution, followed by igniting the sulfide-sulfate precipitate and quenching in water. Before ignition, the precipitate is useless as a pigment, having very little covering power or body. Heating changes its physical character; first, by dehydrating the zinc sulfide; second, by rendering it brittle so that fine grinding is possible; and third, by increasing the density and thereby increasing the body of the pigment.

Since a suitable pigment cannot be prepared by grinding barium sulfate and zinc sulfide together, Mann¹ concludes that lithopone is not a mere mixture. A preparation having the properties of lithopone is formed by mixing a positively charged sol of barium sulfate with a negatively charged sol of zinc sulfide. Mann regards the mechanism of lithopone formation to be a mutual precipitation of oppositely charged colloids. While mutual precipitation of colloidal barium sulfate and colloidal zinc sulfide gives a mixture with the desired physical character, it seems unnecessary to postulate the initial formation of oppositely charged colloidal particles to account for the nature of the product resulting from direct metathesis. The simultaneous condensation of barium sulfate and zinc sulfide molecules from solution will of itself give a more intimate mixture than could result from mutual precipitation of the sols and it is probable that the former process gives the better product. One can obtain a more intimate mixture of barium and strontium carbonates by simultaneous precipitation than could result from grinding the two powders together. Just as in the case of lithopone, the

¹ Colloid Symposium Monograph, 3, 247 (1925).

product resulting from simultaneous precipitation will differ in physical character from the mechanically mixed product; but it would be far fetched to attribute the qualities of the simultaneously precipitated carbonates to mutual precipitation of oppositely charged particles. Moreover, the difficulty of preparing a positively charged hydrosol of barium sulfate precludes the possibility of its formation in the presence of an excess of either sulfate or sulfide ion.¹

The ignition of lithopone in the air results in partial oxidation of the zinc sulfide to zinc oxide. Since the presence of much of the latter decreases the covering power of the pigment, the conditions of ignition are adjusted so as to prevent undue oxidation and the product is quenched in water.² Heating in the absence of oxygen has been suggested;³ but, as will be pointed out later,⁴ the formation of a small amount of oxide on the surface of the zinc sulfide particles is an advantage in increasing the stability of the pigment to light. If the pigment contains too much oxide and is heated too high, it goes off-color, becoming yellowish instead of the desired pure white.⁵

When properly prepared, lithopone is one of the most important white pigments for paints and enamels and for compounding with rubber and linoleum. It is pure white, very fine in texture, and has the same tinctorial strength and greater hiding power than zinc oxide.⁶ Unlike white lead, it is non-poisonous, is unaffected by sulfurous gases, and is stable in every medium for paints except those of high acidity.⁷ It mixes easily with oils and other colors. It is insoluble in water, ammonia, and alcohol and is practically fireproof.⁸

Theoretically, equivalent solutions of barium sulfide and zinc sulfate produce 29.5 per cent zinc sulfide and 70.5 per cent

¹ WEISER: *J. Phys. Chem.*, **21**, 314 (1917).

² O'BRIEN: *J. Phys. Chem.*, **19**, 113 (1915).

³ GRIFFITH: English Patent, 3864 (1877); OSTWALD and BRAUER: German Patent, 202709 (1905).

⁴ See p. 136.

⁵ Cf. MEYER: German Patent, 246021 (1908); BRASE: *Ibid.*, 254291 (1912); ENGLEMANN: *Ibid.*, 264904 (1913); EIBNER: *Ibid.*, 324646 (1918); STEINAU: *Chem. Ztg.*, **44**, 974 (1920); **45**, 741, 1333 (1921).

⁶ TOCH: "Chemistry and Technology of Mixed Paints," 26.

⁷ MORRILL and WADE: "Rubber, Resins, Paints, and Varnishes," 118.

⁸ SCOTT: "White Paints and Painting Material," 237.

barium sulfate. The composition of the commercial products is sometimes modified either by the addition of barytes or of zinc sulfide prior to the ignition. The tinctorial strength and hiding power of the pigment are reduced by adding barytes and are increased by adding zinc sulfide.

Zinc sulfide alone is sometimes employed as a pigment under the name metal white or zinc white, although the latter term is more often applied to the oxide of zinc. When properly prepared, the sulfide possesses good hiding power and, like zinc oxide, is not darkened by the action of sulfur or sulfur vapors. A large number of patents have been taken out for the technical production of the pigment. Thus a fine white product is obtained by the action of sodium sulfide on an alkaline solution of sodium zincate.¹ A powder which does not mat together on drying results if the precipitation is carried out at 195° under pressure.² Good products are reported from the action of sulfur³ or of carbon bisulfide⁴ on an alkaline solution of zinc oxide. It is also obtained from zinc blende or other zinc-bearing ores.⁵ Indeed, zinc blende has been finely pulverized and used directly without further treatment.⁶ It is also formed in the dry way by bringing together the vapors of the two elements and by calcining zinc sulfate under suitable conditions.⁷

A satisfactory pigment must be stable in the light and must possess a pure white color. When formed by precipitation methods, the adsorbed water can be removed only at relatively high temperatures. On ignition in the air, the pigment assumes a yellow color which has been attributed to the formation of an oxysulfide⁸ but which is probably due to zinc oxide, since the

¹ DE STUCKLÉ: German Patent, 171872 (1906).

² GOLDSCHMIDT and SOHN: German Patent, 262701 (1913).

³ PIPEREAUT and VILA: German Patent, 223837 (1907).

⁴ DESACHY: English Patent, 126627 (1919).

⁵ THWAITES: German Patent, 222291 (1908); English Patent, 9174; *J. Soc. Chem. Ind.*, **31**, 431 (1912); CLERC and NIHOUL: German Patent, 381423 (1920).

⁶ RICHTER: *Farben-Ztg.*, **29**, 728 (1924).

⁷ PIPEREAUT and HELBRONNER: U. S. Patent, 1443077 (1918); HELBRONNER: British Patent, 148351 (1920); COMMENT: U. S. Patent, 1374435 (1921).

⁸ DE STUCKLÉ: *J. Soc. Chem. Ind.*, **30**, 96 (1911).

latter is known to be yellow when sintered.¹ The color may be removed² by heating with NH₄HS at 155°; by treating with H₂S in the presence of H₂F₂ or by heating with 2 per cent H₂SO₄.³

THE DARKENING OF ZINC SULFIDE PIGMENTS IN LIGHT

Unless special precautions are taken in the manufacture of zinc sulfide pigments, they blacken in the sunlight and become white again in the dark. Attention was first called to this phenomenon by Phipson⁴ who observed that a gatepost painted white with lithopone turned dark during the day and became white again at night. The barium sulfate in lithopone is without influence or plays but a minor role in the process since zinc sulfide alone will exhibit the same phenomenon. Because of the importance of this behavior from both a theoretical and a technical standpoint, the cause of the blackening and the mechanism of the process will be considered in some detail.

The Cause of the Darkening.—Phipson, who first investigated the darkening of lithopone, claimed that it was not due to the presence of impurities which form black sulfides, and so was led to attribute the discoloration to the presence of a new element, similar to lanthanum, which he named actinium. This hypothesis was disproved by Cawley,⁵ who concluded, by a process of elimination, that the black color resulted from a small amount of finely divided zinc. The first experimental evidence to support this assumption was obtained in Bancroft's laboratory by O'Brien⁶ who brought some of the blackened lithopone in contact with a ferric alum-potassium ferriyanide solution and obtained a blue coloration such as would be expected in the presence of metallic zinc. More recently, Durst⁷ showed that a blackened lithopone became permanently black if brought in contact with a solution of nobler metals such as copper and lead, probably owing to the displacement of the heavy metal from solution by metallic zinc. It should be pointed out, however,

¹ FARNAU: *J. Phys. Chem.*, **17**, 639 (1913).

² DE STUCKLÉ: *J. Soc. Chem. Ind.*, **30**, 96 (1911).

³ KOETSCHET and MEYER: U. S. Patent, 1001415 (1911).

⁴ *Chem. News*, **43**, 283; **44**, 73 (1881).

⁵ *Chem. News*, **44**, 51, 167 (1881); cf. ORR: *Ibid.*, **44**, 12 (1881).

⁶ *J. Phys. Chem.*, **19**, 113 (1915).

⁷ *Z. angew. Chem.*, **35**, 709 (1922).

that this evidence is not altogether conclusive since salts of the noble metals may react with zinc sulfide directly. Thus, silver chloride reacts quantitatively with precipitated zinc sulfide in accordance with the reaction $\text{ZnS} + 2\text{AgCl} \rightarrow \text{ZnCl}_2 + \text{Ag}_2\text{S}$ (black).¹ All doubt as to the cause of the blackening was removed by Job and Emschwiller² who obtained several centigrams of zinc by the action of the light from a quartz mercury lamp on a light-sensitive zinc sulfide suspended in water in a quartz vessel. The metal evolved hydrogen from acids and displaced copper from copper sulfate. Simultaneously with the liberation of zinc, sulfur was formed which was extracted with carbon bisulfide and subsequently crystallized from the solution. Besides the primary products, zinc and sulfur, a small amount of zinc thionate and hydrogen were formed, the latter probably resulting from the slight decomposition of water by the colloidal zinc.

In opposition to the view that the darkening is due to colloidal zinc, Eibner³ claims that the discoloration is caused by the presence of metals which form black sulfides. This view is altogether untenable: first, because chemically pure zinc sulfide is blackened by light;⁴ and second, because the addition to lithopone of metallic salts such as ferric chloride and lead acetate has no appreciable influence on the tendency to darken in light.⁵

Conditions for Photochemical Decomposition.—Zinc sulfide precipitated from ammoniacal solution with hydrogen sulfide or ammonium sulfide consists of minute cubic crystals corresponding to zinc blende or sphalerite. Under ordinary conditions the precipitated sulfide is stable but is rendered light-sensitive by ignition under such conditions that wurtzite is formed. A second requirement for light sensitivity is the presence of an excess of water. Specially prepared, chemically pure zinc sulfide⁶ will darken, so that impurities are not essential to the process, although certain salts, especially soluble zinc salts, increase the light sensitivity. Indeed, an unignited zinc blende formed

¹ JANDER and STUHLMANN: *Z. anal. Chem.*, **60**, 308 (1921).

² *Compt. rend.*, **177**, 313 (1923).

³ *Farben-Ztg.*, **27**, 3378 (1922); *Chem. Ztg.*, **47**, 13 (1923).

⁴ LENARD: *Ann. Physik*, [4] **68**, 553 (1922).

⁵ MAASS and KEMPF: *Z. angew. Chem.*, **36**, 294 (1923).

⁶ TOMASCHEK: *Ann. Physik*, [4] **65**, 189 (1921).

slowly from slightly acid solution will darken on exposure to light in contact with a zinc chloride solution.¹

The much greater light sensitivity of wurtzite was recognized 35 years ago by Cawley,² who pointed out that zinc blende will not darken in ultraviolet light. This conclusion was confirmed recently by Schleede³ from observations with pure precipitated zinc sulfide thrown down from alkaline solution. When ignited below 850° the sulfide was not darkened by long exposure to quartz ultraviolet light and an x-radiogram showed it to consist of the cubic crystals of sphalerite. Ignition at 1150° (35° below the melting point of wurtzite) gave a product with the maximum light sensitivity and an x-radiogram showed it to be hexagonal wurtzite. Ignition at 1000° gave a mixture of both blende and wurtzite which darkened less readily than pure wurtzite. The presence of copper, manganese, or cadmium in amounts necessary to cause phosphorescence had no effect on the light sensitivity.

By carrying out the ignition in the presence of a flux, Schleede found the ignition temperature to be of secondary importance. Thus, when the sulfide was ignited at as low a temperature as 750° in the presence of potassium chloride, an x-radiogram showed the formation of some wurtzite and even glass ultraviolet light caused darkening. Since Schleede did not know the mechanism of the darkening process, he attributed the light sensitivity in the presence of chloride to the formation of mixed crystals of wurtzite and the halogen. Washing out the chloride destroyed the sensitivity to glass ultraviolet light but did not affect the action toward quartz ultraviolet light. Ignition with both chlorides and bromides gave light-sensitive products but ignition with fluorides, phosphates, and borates gave light-stable preparations. This is in line with O'Brien's⁴ findings, that the addition of phosphates, ferrocyanides, borates, cyanides, or bicarbonates to lithopone prevented the darkening or decreased it to an appreciable extent.

Cawley,⁵ who suggested that the darkening of zinc sulfide was due to metallic zinc and who first pointed out that ordinary zinc

¹ WEISER and GARRISON: *J. Phys. Chem.*, **31**, 1237 (1927).

² *Chem. News*, **63**, 88 (1891).

³ *Z. physik. Chem.*, **106**, 391 (1923).

⁴ *J. Phys. Chem.*, **19**, 113 (1915).

⁵ *Chem. News*, **63**, 88 (1891); cf. O'BRIEN: *J. Phys. Chem.*, **19**, 126 (1915).

blende is non-sensitive to light, likewise was the first to recognize the importance of the presence of moisture for the blackening. Recently Lenard¹ and Schleede² called attention to the fact that more than a trace of moisture is necessary. Indeed the blackening is more marked when the surrounding air is supersaturated with moisture than when it is saturated and the effect is still more pronounced when the sulfide is covered with water. The reason for this will be discussed in a later section.

Since the action of light on phosphorescent zinc sulfide is usually accompanied by blackening³ which disappears in the dark, some investigators conclude that the phenomena of luminescence and darkening are intimately related. Thus Job and Emschwiller⁴ give phosphorescence as one of the requirements for a light-sensitive sulfide. Lenard showed, however, that a chemically pure, non-phosphorescent sulfide will blacken in the light and that a fairly dry phosphor will glow without darkening, the latter phenomenon manifesting itself only in the presence of an excess of water vapor. Moreover, the blackening of a number of zinc phosphors was found to require a shorter wave length of light than was needed to excite phosphorescence. Thus the darkening appeared suddenly at a wave length of $334\mu\mu$ while intense phosphorescence maxima were observed by radiations of $430\mu\mu$ and $360\mu\mu$, which caused no darkening. It appears, therefore, that the two phenomena are not necessarily related although they are produced simultaneously by proper excitation. As is well known, the darkening of the silver halides by light is not accompanied by phosphorescence.

Mechanism of the Darkening Process.—Since zinc sulfide which has not been ignited will not blacken ordinarily, Cawley suggests that the ignition results in the formation of some zinc oxide with which the remaining zinc sulfide reacts in the light, as follows: $ZnS + 2ZnO \rightarrow SO_2 + 3Zn$. This view is untenable, since ignition of lithopone under conditions favorable for forming a film of zinc oxide over the sulfide particles gives a light-stable

¹ *Ann. Physik*, [4] **68**, 572 (1922).

² *Z. physik. Chem.*, **106**, 390 (1923).

³ LENARD: *Ann. Physik*, [4] **31**, 652 (1910); BAERWALD: *Ibid.*, [4] **39**, 849 (1912); TOMASCHEK: *Ibid.*, [4] **65**, 195 (1921).

⁴ *Compt. rend.*, **177**, 313 (1923); LOEB and SCHMIEDESKAMP: *Proc. Nat. Acad. Sci.*, **7**, 202 (1921).

product, while removal of the zinc oxide film from such a preparation by heating with an acid, restores the light sensitivity.¹ Furthermore, chemically pure zinc sulfide is darkened by light. Maass and Kempf² believe that the darkening is occasioned by the following reaction: $2\text{ZnS} \rightarrow \text{ZnS}_2 + \text{Zn}$. This is likewise untenable since sulfur instead of the hypothetical zinc disulfide is formed in the process.

Lenard explains the necessity for ignition by postulating the formation of polymerized molecules, $(\text{ZnS})_x$, which are assumed to blacken owing to the "liberation or loosening of zinc atoms from the molecular union." The subsequent discoloration in the dark is attributed to the recombination of the loosened zinc and sulfur atoms. This mechanism is not satisfactory since it is based on some assumptions of doubtful accuracy and since it does not accord with all of the experimental observations. In the first place, the formation of polymerized molecules of zinc sulfide has not been proved. Moreover, it is questionable whether a "loosened" atom of zinc would cause darkening and it is known definitely that free atoms of zinc are formed. Finally, Lenard's assumption that the blackening-discoloration process is reversible, is not in accord with the experimental facts to be recounted in the next section.

It has been known for a long time that a soluble silver salt, such as silver nitrate, increases the light sensitivity of silver bromide³ and Cawley⁴ and O'Brien⁵ observed a very marked increase in sensitivity of lithopone in the presence of soluble zinc salts. The sensitizing action of silver nitrate on silver bromide has been accounted for⁶ by assuming that the soluble salt acts as a bromine acceptor reacting with the latter in accord with the equation: $\text{Br}_2 + \text{AgNO}_3 + \text{H}_2\text{O} = \text{AgBr} + \text{BrOH} + \text{HNO}_3$; but no such mechanism can be assumed for the sensitizing action of

¹ O'BRIEN: *J. Phys. Chem.*, **19**, 113 (1915); MAASS and KEMPF: *Z. angew. Chem.*, **36**, 294 (1922).

² *Loc. cit.*

³ VOGEL: *Pogg. Ann.*, **119**, 497 (1863).

⁴ *Chem. News*, **63**, 88 (1891).

⁵ *J. Phys. Chem.*, **19**, 127 (1915).

⁶ PLOTNIKOW: "Allgemeine Photochemie," 346 (1920).

zinc chloride on lithopone. The recent investigations of Fajans¹ disclose, however, that silver nitrate not only plays the secondary role of a bromine acceptor but it influences the primary light process. The mechanism is as follows: Lottermoser² showed that silver ions from silver nitrate solution are preferentially adsorbed by silver bromide, imparting to the salt a positive charge. Fajans and Frankenburger³ measured this adsorption quantitatively and found that every fourth to tenth atom of bromine in the surface of the silver bromide particles has adsorbed a silver ion from a solution of silver ions as dilute as 1.8×10^{-5} molar. At higher concentrations it is probable that all the bromide atoms in the surface would be covered by adsorbed silver ions giving a crystal with the maximum positive charge.

Since silver bromide crystals belong to the cubic system it may develop its [100] faces only and give cubes or it may develop other faces giving octahedra.⁴ Thus the crystals which form from ammoniacal solution show [111] surfaces only.⁵ The cross-section of a portion of silver bromide particles of the cubic form and of the simplest octahedral form, may be represented diagrammatically as in Fig. 12: (I) when no ions are adsorbed; (II) when every third or fourth bromine atom in the surface has adsorbed a silver ion, and (III) when every third or fourth silver atom in the surface has adsorbed a bromine ion. The silver atoms are designated by +, the bromine atoms by -, and the respective adsorbed ions by Ag' and Br'. Now if one represents by an arrow the point at which an electron from a bromine ion is transferred to the neighboring silver ion, an obvious difference is observed. A smaller amount of energy will be required for the electron transfer and hence the liberation of free silver in the presence of adsorbed silver ion than in a normal surface.

¹ FAJANS and BECKERATH: *Z. physik. Chem.*, **97**, 478 (1921); FAJANS and FRANKENBURGER: *Ibid.*, **105**, 255 (1923); *Z. Elektrochem.*, **28**, 499 (1922).

² *J. prakt. Chem.*, [2] **72**, 39 (1905); **73**, 374 (1906); *Z. physik. Chem.*, **60**, 451 (1907); **70**, 239 (1910).

³ *Z. physik. Chem.*, **105**, 255 (1923).

⁴ Cf. SHEPPARD and TRIVELLI: Eder, "Ausführliches Handbuch der Photographie, Grundlage des Negativeprozesses," 735 (1926).

⁵ Cf. FAJANS and FRANKENBURGER: *Z. physik. Chem.*, **105**, 263 (1923).

I. Before adsorption of any ions:

Cubic [100]							Octahedral [111]						
+	-	+	-	-	+	-				+	-		
-	+	-	+	-	+				+	-	+	-	↓
+	-	+	-	+		↓			+	-	+	-	+
-	+	-	+	-	+				-	+	-	+	+
+	-	+	-	+	-				-	-	+	-	+
-	+	-	+	-	+				-	+			

II. After adsorption of silver ions:

		Ag'											
+	-	+	-	+	-				+	-			Ag
-	+	-	+	-	+				+	-	r		
+	-	+	-	+	-	Ag'			+	-	+	-	+
-	+	-	+	-		r			+	-	+	-	+
+	-	+	-	+			Ag'		+	-	+	-	+
-	+	-	+	-	r				-	+	-	r	
+	-	+	-	+					-	+	-	r	
-	+	-	+	-	+				-	+			
		Ag'											

III. After adsorption of bromine ions:

		Br'											
+	-	+	-	+					+	-			
-	+	-	+	-	r				+	-	+	-	
+	-	+	-	+	-				+	-	+	-	
-	+	-	+	-	+	Br'			-	+	-	r	-
+	-	+	-	+	-				-	+	-	+	Br'
-	+	-	+	-	+				-	+	-	+	
		Br'											

FIG. 12.—Position of adsorbed ions on the silver halide lattice.

Since both zinc and sulfur are obtained by the photochemical decomposition of a sensitive sulfide, it would seem that, as in the case of silver bromide, the primary process consists in an exchange of the electrostatic charges of the ions with the liberation of the free elements. Analogous to the behavior of the silver halide in the presence of adsorbed silver ion, it follows that adsorbed zinc ions will cut down the energy required to decompose zinc sulfide and liberate the atoms of which it is composed. Since a salt always shows a strong tendency to adsorb its own ions, there is little doubt but that zinc ions will be preferentially adsorbed at a zinc sulfide surface, just as silver ions are adsorbed at a silver halide surface. From this point of view, any factor which favors the formation of zinc ions in the immediate region of the surface of zinc sulfide will tend to increase its sensitivity toward light. As a matter of fact, soluble zinc salts have a pronounced sensitizing action, whereas insoluble zinc salts have little effect; moreover, ignition in the presence of a small amount of chloride or bromide which form soluble zinc salts favors the blackening while ignition with flourides, phosphates, or borates which form insoluble salts, retards or prevents blackening.¹

The Role of Water.—From the above consideration it follows that the role of water in the photochemical decomposition of zinc sulfide is merely that of an ionizing solvent for the sulfide and for adsorbed zinc salts, yielding zinc ions which are adsorbed on the surface of the sulfide lattice and sensitize it. As has been pointed out, natural zinc blende and precipitated blende are ordinarily light stable whereas wurtzite is decomposed by ultraviolet light. The difference in behavior is readily understood when one recalls that wurtzite is 4.5 times as soluble as blende.² This means not only that the stability of the wurtzite lattice is the smaller but that it yields more readily the zinc ions which play such an important part in the darkening process.

Since a solution of a suitable acid or zinc salt increases the sensitivity of wurtzite enormously, it seemed likely that precipitated zinc sulfide might be made to darken under suitable conditions. This proved to be the case.³ A 20 per cent solution of

¹ See also p. 136.

² GMELIN: "Handbuch anorg. Chem.", 8th ed., **32**, 201 (1924).

³ WEISER and GARRISON: *J. Phys. Chem.*, **31**, 1242 (1927).

recrystallized zinc sulfate was treated with ammonia short of precipitation, and a stream of specially purified hydrogen sulfide¹ was passed into the solution very slowly until precipitation ceased. In this way, fairly large crystals were formed in the presence of an excess of zinc ion since the precipitation was incomplete, stopping when the hydrogen ion concentration became too high. After freeing the sulfide from excess sulfate, it was exposed to quartz ultraviolet light in contact with zinc chloride; and prompt blackening resulted. A sample of the gelatinous sulfide precipitated rapidly with ammonium sulfide did not blacken in the presence of zinc chloride. A distinct crystal structure is therefore essential to light sensitivity.

Since the preferential adsorption of zinc ion sensitizes the sulfide, it seemed likely that the presence of a salt yielding an anion which is more readily adsorbed than the cation would stabilize the sulfide. Referring once more to the case of silver bromide, it would appear from (III), page 130, that adsorbed bromide ion would tend to stabilize the lattice, since the passage of an electron in the direction of the arrow would be opposed by the electrostatic repulsion of the adsorbed ion. Fajans and Steiner² believe that adsorbed bromide ion should sensitize the lattice since it is reasoned that an electron should pass from the adsorbed bromide ion to the silver with a smaller expenditure of energy than from a bromide ion in the lattice. It should be pointed out, however, that the transfer of an electron from the adsorbed ion will be opposed by the electrostatic repulsion of five bromide ions surrounding the silver ion in the surface of the lattice while the passage of an electron from a bromide ion to the silver in a normal surface will be opposed by the electrostatic repulsion of but four ions. It therefore becomes a question of fact whether the adsorbed bromide ion will sensitize the normal lattice, stabilize the normal lattice, or have no measurable effect. Frankenburger³ found the spectrum sensitivity threshold to lie between 410 and $435\mu\mu$ for a slightly acid silver bromide containing adsorbed bromide ion and for a pure dry silver bromide formed by the action of bromine on a silver plate and illuminated

¹ LENZ: *Z. anal. Chem.*, **22**, 393 (1883).

² *Z. physik. Chem.*, **125**, 307 (1927).

³ FAJANS and FRANKENBURGER: *Z. physik. Chem.*, **105**, 255 (1923).

in a vacuum. The failure of the adsorbed bromide ion to sensitize the silver salt was attributed by Frankenburger to the desensitizing action of hydrogen ion adsorbed on the adsorbed bromide. Later Steiner¹ found that the sensitivity of a salt with adsorbed bromide was the same in acid and in neutral solution. From these observations one would conclude that the sensitivity of the normal lattice is neither increased nor decreased by adsorbed bromide ion. In some preliminary experiments it was found, however, that a sample of silver bromide washed repeatedly by the aid of the centrifuge is darkened slightly less rapidly when suspended in silver bromide solution than when suspended in water. This is in line with Wetzlar's² observation of a century ago that silver chloride darkens less rapidly in sodium chloride solution than in water.

Although the light sensitivity of silver bromide is not greatly altered in potassium bromide solution, that of zinc sulfide is decreased enormously in a sodium sulfide solution. Thus a sensitive sulfide covered with water was blackened by a 2-minute exposure to quartz ultraviolet light while the same preparation covered by a sodium sulfide solution as dilute as *N*/50 showed no signs of blackening after a 30-minute exposure to quartz ultraviolet light of the same intensity. Sodium sulfate and borax likewise have a stabilizing influence. In general, any salt with a readily adsorbed anion will tend to stabilize the sulfide, Nishizawa³ found that the sulfide was stabilized by glycerin, hydroxides, and the salts and esters of tartaric and polyhydroxy-stearic acids. The stabilization was due to the strongly adsorbed anions of these compounds, but this was not understood by Nishizawa.

In addition to its action as an ionizing solvent, water may be assumed to have a purely mechanical effect, forming a film around the liberated zinc, thereby preventing its oxidation by oxygen, ozone, or the liberated sulfur. This effect must be slight, however, since other liquids which wet either zinc or sulfur are without influence on the darkening. Since an excess of water is essential for darkening, it is improbable that the liquid plays a

¹ *Z. physik. Chem.*, **125**, 275 (1927).

² *Pogg. Ann.*, **9**, 172 (1827).

³ *J. Tokoyo Chem. Soc.*, **41**, 1054 (1920); *Chem. Abstr.*, **15**, 1407 (1921); British Patent, 156971 (1919).

catalytic role similar to that in the thermal decomposition of ammonium chloride.¹ Maass and Kempf² postulate a reducing action of nascent hydrogen formed by photochemical decomposition of the required water.³ This assumption seems far fetched, since either nascent oxygen⁴ or hydrogen peroxide⁵ will be formed simultaneously and will neutralize any effect of hydrogen. It is further suggested that formaldehyde,⁶ formed by the action of light on moist carbon dioxide, accelerates the reduction. This view is likewise untenable since the blackening goes on in the absence of carbon dioxide.⁷ Since Maass and Kempf were the first to suggest that adsorbed zinc ion might sensitize zinc sulfide in the same way that adsorbed silver ion sensitizes silver bromide, one is at a loss to know how they happened to overlook the true role of water in the darkening process.

The Decolorization Process.—The decolorization of blackened zinc sulfide or lithopone takes place in the dark only in the presence of oxygen or some oxidizing agent such as chlorine, ozone, or hydrogen peroxide. It is obvious, therefore, that the process is only partly reversible if at all, the decolorization in the air being due to the oxidation of the finely divided metal to white zinc oxide or basic carbonate.⁸ As already mentioned, Lenard's⁹ view is that the photochemical process is reversible. This is based on his observation that a sulfide thrice darkened and allowed to whiten appears to be as sensitive as the original preparation. Apparently, Lenard started out to prove that the reaction is reversible or he would not have been content with three repetitions. Such a small amount of decomposition takes place that the darkening and decolorization must be repeated a number of times before a marked decrease in sensitivity is noted. Phipson reports that his classic gatepost, painted with lithopone,

¹ BAKER: *J. Chem. Soc.*, **65**, 611 (1894).

² Z. *angew. Chem.*, **36**, 294 (1923).

³ BERTHELOT and GAUDECHON: *Compt. rend.*, **150**, 1690; **151**, 395 (1910).

⁴ THIELE: *Ber.*, **40**, 4914 (1907).

⁵ KERNBAUM: *Compt. rend.*, **152**, 1668 (1911).

⁶ BERTHELOT and GAUDECHON: *Compt. rend.*, **150**, 1169, 1327, 1517, 1690 (1910).

⁷ WEISER and GARRISON: *J. Phys. Chem.*, **31**, 1239 (1927).

⁸ O'BRIEN: *J. Phys. Chem.*, **19**, 113 (1915).

⁹ *Ann. Physik*, [4] **68**, 553 (1922).

becomes alternately dark in the daytime and white at night for a long time; but at last, it remains white. The permanent white color on prolonged ageing is probably due to a protecting film of oxide or basic carbonate. There is apparently no oxidation of the zinc sulfide to zinc sulfate.¹

Convinced that the photochemical process is reversible, Lenard assumes that discoloration in the presence of oxygen, chlorine, ozone, or hydrogen peroxide is due to the catalytic action of the oxidizing agent on the recombination of zinc and sulfur. This view is absurd, since everyone knows that zinc reacts more readily with chlorine or ozone than with sulfur. Lenard recognizes this condition but gets around it by saying that the zinc atoms which cause the darkening are merely "loosened," whereas we know definitely that the blackening is caused by free zinc.

PREVENTION OF DARKENING OF ZINC SULFIDE PIGMENTS

From a technical standpoint, it is of particular importance to prepare lithopone under such conditions that it is not appreciably discolored by light. From what has been said in the preceding section the following general rules may be deduced: (1) carry out the necessary ignition so that light-sensitive wurtzite is not formed; (2) avoid the presence of soluble zinc salts which increase the light sensitivity; (3) add a salt with a highly adsorbed anion; (4) treat the pigment so as to produce a film of oxide or other light-stable solid around the zinc sulfide particles.

Theoretically, the simplest procedure would seem to consist in ignition of the pigment below the temperature where wurtzite is formed. This is apparently what is done by the New Jersey Zinc Company.² It is claimed that the lithopone should be precipitated in the presence of chloride in order to get a commercial product with the desired covering power and oil-adsorbing qualities. Variation in the amount of chloride has a marked influence on the ignition temperature which must be employed to get the desired physical character. But as already shown, the presence of chloride decreases the stability of the pigment toward

¹ WOLFF: *Z. angew. Chem.*, **37**, 333 (1924).

² BREYER, CROLL, FARBER, and SINGMASTER: U. S. Patent, 1411645 (1922); BREYER and FARBER: *Ibid.*, 1446637 (1923).

light,¹ probably owing to the formation of some soluble zinc chloride during ignition. Extended observations disclose that the ignition temperature curves of covering power and oil adsorption on the one hand, and of light stability on the other, cut each other. Hence, to obtain a lithopone that is at once the most light stable and has the highest covering power, the amount of chloride and the ignition temperature should correspond to the point of intersection of the curves. Thus, for a lithopone precipitated from a zinc sulfate solution (density 1.16) containing not more than 2 grams of chlorine per liter, the best ignition temperature is between 700 and 800°. Under these conditions it is probable that the chief product is the light-stable blende. A rigid control of the ignition temperature is essential for a uniform product.² It would seem that the addition of a salt with a strongly adsorbed anion would destroy the light sensitivity of any wurtzite that was formed.

Attention has been called to the spontaneous formation of a protecting film around the sensitive zinc oxide particles by repeated darkening and discoloration in air. It is, of course, impractical to form a protecting film in this way, but most of the earlier methods for obtaining light-proof lithopones involve the addition of an oxidizing agent or some salt that will yield an insoluble protecting film.³ Recent recommendations involve a similar principle. For example, Kuzell⁴ sprays lithopone in the air to oxidize the zinc sulfide superficially to zinc oxide. Thus, by igniting lithopone so that little wurtzite is formed or by protecting the light-sensitive sulfide with a strongly adsorbed anion or a non-sensitive film, products are obtained which appear to meet all of the technical requirements.

¹ ROCHE: *Rev. chim. ind.*, **31**, 109 (1922); STEINAU: *Chem. Ztg.*, **45**, 741 (1921).

² SINGMASTER and BREYER: U. S. Patent, 1411646 (1922); SINGMASTER, BREYER, and FARBER: *Ibid.*, 1411648 (1922).

³ O'BRIEN: *J. Phys. Chem.*, **19**, 113 (1915); CAWLEY: *Chem. News*, **63**, 88 (1891); ALBERTI: *Chem. Zentr.*, II, 651 (1906); STEINAU: *Ibid.*, I, 1593 (1908); OSTWALD and BRAUER: *Ibid.*, II, 1707 (1908); ALLENDORFF: *Ibid.*, I, 116 (1909); BRASE: German Patent, 254291 (1912).

⁴ U. S. Patent, 1399500 (1922); cf., also, NISHIZAWA: *J. Tokoyo Chem. Soc.*, **41**, 1054 (1920); British Patent, 156971 (1915).

CHAPTER IX

FLOTATION OF ORES

The concentration of ores by flotation is used chiefly for the separation of sulfides from the siliceous gangue with which they are usually associated. The operation depends on the property of finely divided particles of the sulfides to concentrate preferentially at an interface. The principles underlying the several processes will be discussed in some detail.

THE BULK-OIL PROCESS

The bulk-oil process of ore flotation invented by Elmore in 1898 is of interest theoretically although it is no longer used technically. The process depends on the fact that some sulfide ores suspended in water can be removed from the water phase by shaking with suitable oils, while the gangue remains in the aqueous phase.

A solid adheres to a liquid which adsorbs or wets it. With two immiscible liquids and one solid, selective adsorption comes in which leads to varying results as found by Hofmann¹ and Reinders.² Thus, if finely divided gypsum is shaken with water and benzene or chloroform, the solid remains in the water; red lead, on the other hand, adheres to the surface of the organic liquid. In general, the solid particles tend to go into the water phase if they adsorb water to the practical exclusion of the organic liquid; they tend to go into the organic liquid if they adsorb the latter to the practical exclusion of the water; and they tend to go into the dineric interface if the adsorption of the two liquids by the solid is sufficiently great to increase considerably the miscibility of the two liquids at the surface between solid and liquid.³

¹ *Z. physik. Chem.*, **83**, 385 (1913).

² *Kolloid-Z.*, **13**, 235 (1913).

³ BANCROFT: *J. Phys. Chem.*, **19**, 287 (1915); DES COUDRES: *Arch. Entwicklungsmechanik*, **7**, 325 (1898).

The difference in behavior of a number of solid substances when shaken with two liquids is shown in Table XX taken from observations by Reinders. In this table the letters *w*, *o*, and *i* mean that practically all of the solid goes to the water, the organic liquid, and the interface, respectively. Two letters such as *wi* mean that the powder goes chiefly to the water phase, but a part of it goes to the interface; while *w(i)* means that a very little goes to the interface.

TABLE XX.—PREFERENTIAL ADSORPTION OF SOLIDS BY LIQUIDS

Suspended material	Water and				
	Paraffin oil	Amyl alcohol	CCl ₄	C ₆ H ₆	(C ₂ H ₅) ₂ O
Kaolin.....	<i>w</i>	<i>w(i)</i>	<i>w(i)</i>	<i>w</i>	<i>w(i)</i>
CaF ₂	<i>wi</i>	<i>wi</i>	<i>w(i)</i>	<i>w(i)</i>	<i>w(i)</i>
Gypsum.....	<i>w</i>	<i>wi</i>	<i>w</i>	<i>iw</i>	<i>wi</i>
BaSO ₄	<i>w(i)</i>	<i>wi</i>	<i>wi</i>	<i>wi</i>	<i>wi</i>
PbO.....	<i>i</i>	<i>i</i>	<i>iw</i>	<i>i</i>	<i>iw</i>
Malachite.....	<i>io</i>	<i>i</i>	<i>i</i>	<i>i</i>	<i>iw</i>
ZnS.....	<i>i</i>	<i>i</i>	<i>i</i>	<i>i</i>	<i>iw</i>
PbS.....	<i>io</i>	<i>io</i>	<i>i</i>	<i>i</i>	<i>i</i>
C.....	<i>io</i>	<i>i</i>	<i>i</i>	<i>i</i>	<i>i</i>
As ₂ S ₃ (sol).....	<i>i</i>	<i>w</i>	<i>w</i>	<i>w</i>

These observations illustrate the tendency for the sulfides to go into the dineric interface; on the other hand, the gangue material, such as kaolin and gypsum, tends to remain in the aqueous phase. Carbon tends to go into the interface. Recently a flotation process has been used to get ash-free coal which yields a new coke possessing extraordinary properties.¹ Colloidal sulfides such as those of zinc, gold, and copper are coagulated by shaking with chloroform or benzene, and subsequently concentrate in the dineric interface² just as does colloidal arsenic trisulfide on shaking with amyl alcohol.

¹ BURY, BROADBRIDGE, and HUTCHINSON: *Trans. Inst. Mining Eng. (London)* **60**, 243 (1921).

² YANEK: *Ann. école mines Oural*, **1**, 45 (1919); *Chem. Abstr.*, **15**, 1239 (1921).

It should be pointed out that the conclusions as to the way a given pair of liquids will behave with a given solid depend on the experimental conditions such as the liquid which wets the solid first, the relative amounts of the liquids, and the time allowed for equilibrium conditions to be set up. Thus, Hofmann found that glass is wetted more readily and more rapidly by water than by xylene or petroleum but that an excess of the organic liquid will in time displace a film of water from a glass surface. Accordingly, one would expect glass powder to behave differently depending on whether it was treated first with water or with the organic liquid. Actually, if the glass is first wetted with water and then shaken with kerosene, all the glass goes into the water phase, whereas if the powder is allowed to stand for a long time with kerosene or heated with it to hasten the removal of the air film, some of the glass is carried into the interface and remains there for some time.

It is the opinion of Sulman,¹ Edser,² and others that the flotation process does not depend alone on relative adsorbability or wettability, that is, on the fact that the gangue which is more easily wetted by water goes to the water phase while the sulfide particles which are wetted by water with difficulty, go to the interface especially if covered with a film of oil. In addition, there is assumed to be partial wetting or the existence of a contact angle between solid and liquid which undergoes hysteresis, that is, changes gradually until a condition of equilibrium is reached. From this point of view, a large hysteresis of the contact angle means that any surface of a solid covered by an air film will not be wetted immediately although this will happen after a time; a slight hysteresis, on the other hand, means that wetting corresponding with equilibrium conditions is attained promptly. Favorable flotation conditions are obtained by choosing the oil and the electrolytes added to the aqueous phase, so that the hysteresis is as large as possible in the case of the sulfide and as small as possible in the case of the gangue.

Until we know with certainty that there is a definite contact angle under equilibrium conditions, one is hardly justified in

¹ *Bull. Inst. Mining Met.*, **29**, 44 (1920).

² "Brit. Assocn. Advancement Sci., Fourth Rept. on Colloid Chemistry," 263 (1922).

attributing the slow displacement of a film of gas or liquid by another liquid to large hysteresis of an alleged contact angle. On the basis of adsorption, the contact angle should be zero and it has been found experimentally to be zero whenever equilibrium conditions are definitely reached and the measurements are made with a high degree of accuracy.¹

In the Elmore bulk-oil process, the pulverized ore was first mixed with a considerable quantity of water and then shaken with a highly viscous oil. The mixture was allowed to stand until the water and sand subsided and the oil with its charge of sulfide particles floated to the top. The process was expensive technically, requiring approximately 1 ton of oil per ton of ore. It has therefore been entirely replaced by cheaper and more efficient processes, the most important of which is the frothing process.

THE FROTHING PROCESS

The development of successful processes of oil flotation dates from Froment's discovery in 1901² that when small quantities of oil and acid are agitated in water, the sulfide particles attach themselves to oiled gas bubbles and float to the surface as a froth while the gangue sinks to the bottom of the container. To get sufficient froth, Froment added small amounts of calcite which reacted with acid to give bubbles of carbon dioxide. Elmore in 1904 accomplished a similar thing by applying a vacuum to the pulp and warming, thereby liberating bubbles of air which float up the oiled particles. Both of these methods of obtaining the desired froth have been superseded by the more satisfactory process of violent agitation with air.

The importance of the froth or foam in flotation practice calls for special considerations of the conditions of froth formation and the mechanism by which the ore is concentrated in the froth system.

¹ RAYLEIGH: *Scientific Papers*, **3**, 393, 420 (1902); RICHARDS and CARVER: *J. Am. Chem. Soc.*, **43**, 827 (1921); cf., however, SULMAN: *Bull. Inst. Mining Met.*, **29**, 44 (1920); BOSANQUET and HARTLEY: *Phil. Mag.*, [6] **42**, 456 (1921).

² British Patent, 12778 (1902); cf., also, EVERSON: U. S. Patent, 348157 (1886); DELPRAT: *Ibid.*, 735071 (1903).

FROTH OR FOAM

The Foam Former.—A froth or foam consists of bubbles of gas surrounded by a more or less viscous film. To get a foam on shaking a fluid with air, it is essential, therefore, that there be a surface film, in other words, that the concentration in the surface shall differ from the concentration of the body of the liquid.¹ In general, a pure liquid will not foam but all true solutions will foam provided there is a definite increase or decrease of surface

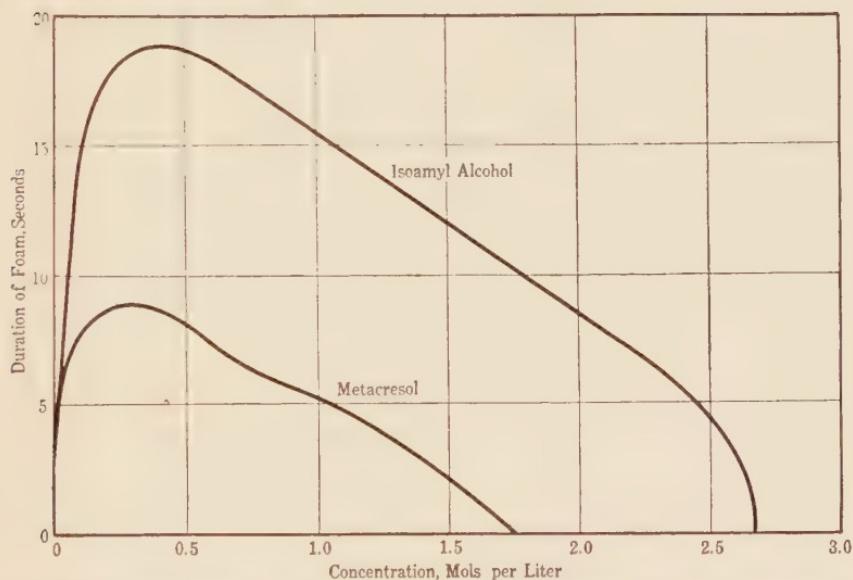


FIG. 13.—Influence of the concentration of foam former on the duration of foam.

tension with concentration. Similarly, a sol will foam provided the colloidal particles concentrate in the interface or are forced out of the interface.

Aqueous solutions of the foam-forming material exhibit an optimum concentration at which the foam is most stable. This is illustrated by the curves of Fig. 13 in which the concentration of the solution is plotted against the duration of the foam which results on shaking 10 cubic centimeters of solution in a cylindrical tube 25 centimeters long and 1.5 centimeters inside diameter.²

¹Cf. FOULK: *J. Am. Water Works Assoc.*, **17**, 160 (1927).

²BARTSCH: *Kolloidchem. Beihefte*, **20**, 3 (1925).

Contrary to what one might expect, the maximum stability is attained at a relatively low concentration of isoamyl alcohol and m-cresol. This is not unusual, as will be seen by referring to Table XXI which records the maximum duration of the foam obtained with a number of alcohols and acids, and the concentration and surface tension of the solution giving the most stable froth. It is rather surprising that the critical concentration of the several solutions possesses surface tensions which are not far apart. So far as these observations go, however, it appears that the solutions with the lowest surface tension give the most durable foam.

TABLE XXI.—PROPERTIES OF SOME FOAM-FORMING SOLUTIONS

Aqueous solution of	Duration of foam, seconds	Optimum concentration for most stable foam, mols per liter	Surface tension at optimum concentration, dynes per centimeter
Ethyl alcohol.....	5	0.28	66
Propyl alcohol.....	11	0.32	56
Isobutyl alcohol.....	12	0.09	56
Isoamyl alcohol.....	17	0.036	54
Tertiary amyl alcohol.....	10	0.034	61
Heptyl alcohol.....	8	0.0007	68
Octyl alcohol.....	5	0.0003	64
Formic acid.....	4	0.45	70
Acetic acid.....	8	0.20	69
Propionic acid.....	11	0.25	61
Butyric acid.....	18	1.00	33
Valeric acid.....	9	0.015	64
Caproic acid.....	13	0.0075	57
Heptylic acid.....	16	0.0015	60
Caprylic acid.....	12	0.00025	66
Nonylic acid.....	5	0.00007	70
Benzyl alcohol.....	10	0.10	59
Meta-cresol.....	9	0.025	62
Anilin.....	11	0.10	62
Para-toluidine	6	0.04	63

Foam formers are most frequently substances in true solution which lower the surface tension and therefore concentrate in the

surface film. In practice they are usually non-electrolytes slightly soluble in water. An insoluble substance such as oleic acid may act as a foam former provided it emulsifies with the water. Colloidal frothers like the soluble frothers show an optimum in the foam-forming capacity at some fairly definite concentration. Thus oleic acid gives a foam with the maximum duration of 9 minutes when the emulsion contains 0.5 per cent of the oil.

The Foam Stabilizer.—For a fairly permanent foam, the film must be sufficiently viscous in itself or must be stabilized by introducing finely divided solids into the interface. In general, soap solutions give quite stable foams owing to the relatively high viscosity of the soap film. The addition of glycerin, which is frequently recommended for making good soap-bubble solutions, acts by increasing the viscosity of the liquid and by making the surface films soft and flexible. Saponin solutions give more rigid bubbles than soap.¹

As we have seen, aqueous solutions of ethyl alcohol and of acetic acid will foam, but the films are too fragile for the foam to last. Such foams will be stabilized by adding a solid powder which will go into the interface making a viscous film. Thus lampblack will stabilize an acetic acid foam and lycopodium powder an alcohol foam. Beer gives a stable froth because of the presence of colloidal albumoses which concentrate in the interface.² Ferric acetate froths readily³ because of hydrolysis with the liberation of acetic acid, a froth former, and of hydrous ferric oxide which is adsorbed at the interface and stabilizes the froth.

The amount of solid which concentrates in the foam film and the stability of the foam depend on the nature of the solid particles, the degree of subdivision of the particles, and the concentration of the solution. Thus, gangue materials, such as feldspar and quartz, have little or no effect on the stability of an isoamyl alcohol foam; on the other hand, sulfide ores such as chalcopyrite, zinc blende, molybdenite, and galena have a marked stabilizing action.

¹ BOYS: "Soap Bubbles," 2nd ed. (1912).

² ZEIDLER and NAUCK: *J. Soc. Chem. Ind.*, **20**, 269 (1901).

³ GLADSTONE: *Phil. Mag.*, [4] **14**, 314 (1857).

The degree of subdivision of the solid is extremely important. Thus, galena particles varying in size from 900 to 2500 sieve-meshes per square centimeter¹ increase the duration of an isoamyl alcohol foam from 17 seconds to 60 seconds; while the stability is increased to several hours by galena particles between 9000 and 12,000 sieve-meshes per square centimeter in size.

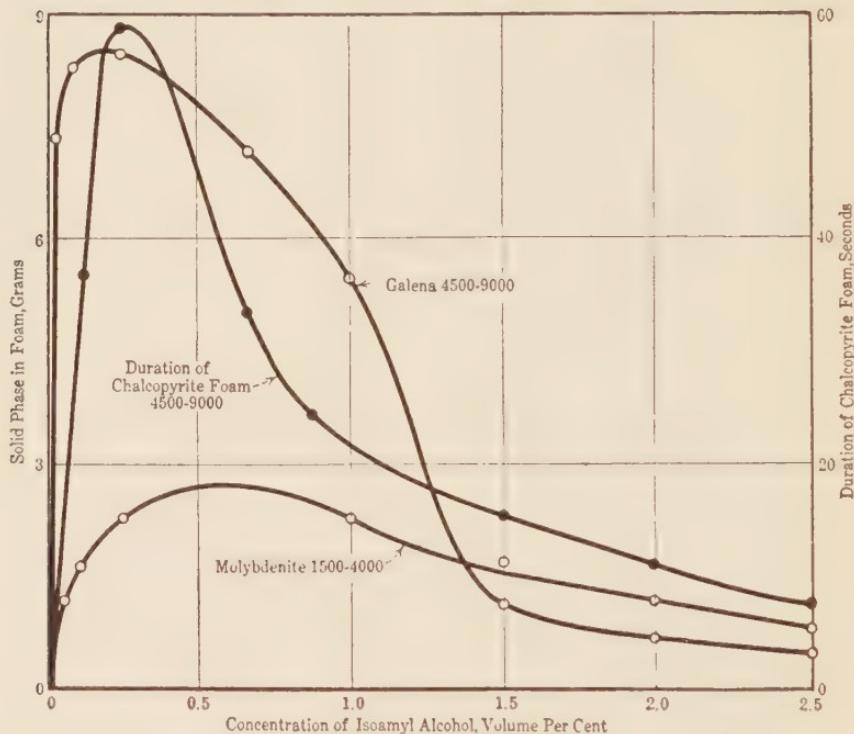


FIG. 14.—Influence of concentration of isoamyl alcohol (1) on the amount of solid phase in the foam and (2) on the duration of foam.

The effect of concentration of the foam-forming solution is illustrated in Fig. 14² which shows the influence of the isoamyl alcohol concentration (1) on the amount of galena and of molybdenite found in the foam and (2) on the duration of a foam containing chalcopyrite. It will be seen that the amount of solid going into the foam and the stability of the foam pass through a maximum with increasing concentration of the alcohol. The

¹ This manner of expressing size of particles means that the particles will pass a sieve containing the specified number of meshes per square centimeter.

² BARTSCH: *Kolloidchem. Beihefte*, **20**, 25 (1925).

maximum in both types of curve corresponds approximately to the concentration of isoamyl alcohol which gives the most stable foam in the absence of a solid. The importance of a recognition of this behavior for technical ore flotation is obvious.

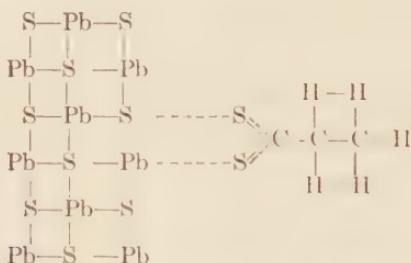
The Collector.—If a small amount of an insoluble oil such as oleic acid is shaken with water, bubbles of air are formed which are coated with a thin film of oil around which is water. Here also the oil film is not viscous enough to form a stable froth but if a pulverized sulfide ore is introduced into the mixture, the solid sulfide particles concentrate in the interface giving a stable froth of "armored" bubbles which can be scraped off. The Minerals Separation Company took out patents in 1905 for the flotation of ores by the use of a fraction of 1 per cent of an oil such as oleic acid. An oil containing some soluble constituent which acts as froth former gives better results than a straight insoluble oil. Thus, the addition of isoamyl alcohol to water before shaking with oleic acid and sulfide particles yields a much stabler foam than oleic acid and sulfide particles alone. Similarly, kerosene alone does not froth with water and the foam formed by adding fine particles which are wet by kerosene is relatively unstable; but if a small amount of cresol, a foam former, is dissolved in the water before adding the kerosene and solid particles, a fairly stable foam results.

Substances, such as oleic acid and kerosene, which are effective in carrying certain solid particles into the interface are called collectors. The best collecting oils are liquids at the temperature employed in flotation practice. A number of oils, particularly many of the Australian eucalyptus oils, possess the properties of both frothers and collectors. The eucalyptus oils consist mainly of dextra-pinene and phillandrene. If the content of the latter is relatively low, the addition of mineral oil or oleic acid is necessary to get satisfactory results. In America the use of pine oil or pine tar oil has proven satisfactory with or without the admixture of such substances as mineral oils, alpha-naphthylamine, and potassium xanthate.

The highly soluble potassium xanthate affects the surface tension very slightly even at a concentration well beyond that employed in flotation practice. It must act, therefore, as a collector and not as a foam former. The xanthate is adsorbed

much more strongly by certain sulfide particles and is a much better collector than the slightly soluble thiocarbanilide which is similar chemically. Since this is diametrically opposed to the rule that among chemically similar substances, the least soluble is the most strongly adsorbed, Gaudin¹ suggests that the adsorption of xanthate ion from the potassium salt is followed by a reaction with the base-metal atom at the surface of the mineral, forming insoluble xanthates.

Such an explanation as this, however, is not entirely satisfactory; for if the formation of base-metal xanthates were alone involved, the xanthates should float insoluble sulfates, carbonates, etc., of the metals whose sulfides are floated. This is not the case; even large quantities of xanthate (several pounds per ton) do not succeed in floating these minerals. On the other hand, metal powders are floated by the xanthates, although not nearly as well as the sulfides. The well-known fact that sulfides tend to form polysulfides such as K_2S_5 , suggests the possibility of the formation, as a surface compound, of a polysulfide having a structure



This hypothesis involves the breaking up of the $C = S$ and $C - S$ valence links into two $C \cdots S$ links; that is, the setting up of a tautomeric valence shifting within the group CSS . Explanations of this type are not infrequent in the field of organic chemistry.

This hypothesis explains the fact that pyrites, which has more sulfurs than other sulfides, is the most floatable of sulfides; that zinc, the xanthate of which is comparatively soluble, is the least floatable of the sulfides; that non-sulfides of the base metals are non-floatable, and that the base-metal powders float indifferently with the xanthates as collectors.

Since the alleged metallic polysulfides are not definite compounds as a rule, it seems altogether probable that the polysulfides which Gaudin assumes, are adsorption complexes rather than Dalton compounds. In any event, the coated particles are more

¹ *Mining Met.*, 8, July (1927).

strongly adsorbed than the uncoated particles at the air-liquid interface which constitutes the foam, and so the former are floated more readily.

Suitable oils and potassium xanthate are called collectors because their adsorption by the solid particles causes the latter to concentrate in the foam film. Since this results in a stabilization of the foam, the collector is sometimes referred to as a foam stabilizer. It seems best, however, to reserve the term stabilizer for the solid particles which armor plate the bubbles.

The role of a collector in froth floatation is shown by some observations of Bartsch¹ on the composition of foams formed by shaking sulfide ores with 0.25 per cent solution of isoamyl alcohol containing varying amounts of oleic acid (Table XXII). More

TABLE XXII.—CONCENTRATION OF SOLID PHASE IN FOAM

Mineral	Particle size in sieve-meshes per square centimeter	Weight of solid in the foam		
		Oleic acid concentration in mols		
		0.0000	0.000025	0.0003
Chalcopyrite.....	600- 1,600	0.64	3.42	3.91
	1,600- 4,000	1.04	4.29	5.30
	4,000- 9,000	1.30	4.75	6.43
	9,000-12,000	1.65	5.06	7.08
Molybdenite.....	600- 1,600	2.69	2.98	2.73
	1,600- 4,000	2.29	2.45	2.18
	4,000- 9,000	1.73	2.08	2.03
	9,000-12,000	1.43	1.48	1.83
Zinc blende.....	600- 1,600	0.81	2.94	0.85
	1,600- 4,000	1.54	3.90	1.52
	4,000- 9,000	2.30	6.75	3.97
	9,000-12,000	2.48	6.83	6.33
Galena.....	600- 1,600	0.23	2.88	0.39
	1,600- 4,000	3.28	6.84	0.98
	4,000- 9,000	6.04	9.35	2.24
	9,000-12,000	7.91	10.49	3.14

¹ *Kolloidchem. Beihefte*, **20**, 28 (1925).

extended observations with galena are shown graphically in Fig. 15. It will be seen that the amount of solid which goes into the foam varies with the nature of the sulfide. In all cases, there is an optimum concentration of oleic acid for the best flotation but the optimum likewise varies with the nature of the sulfide. In general, the amount of oleic acid required increases with the degree of subdivision above a certain point. Thus the

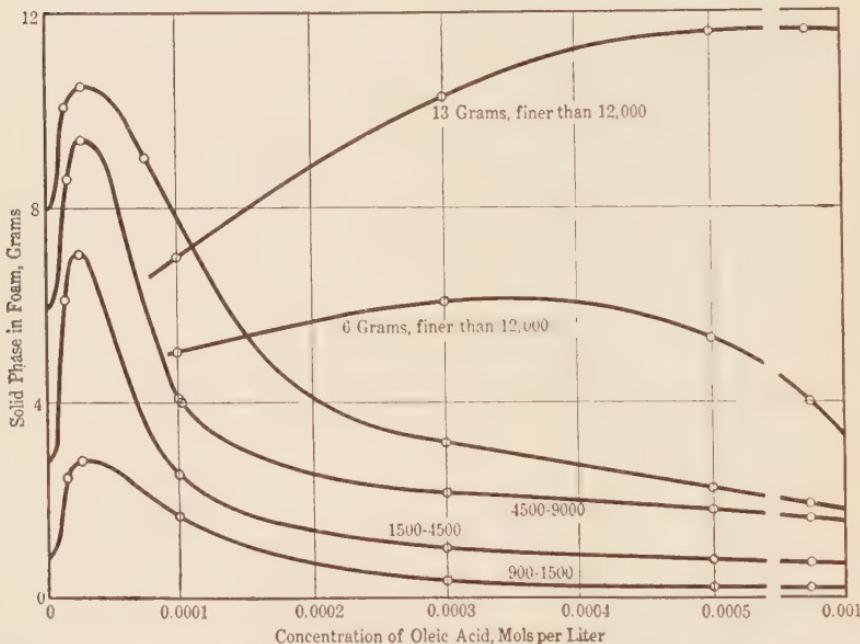


FIG. 15.—Influence of the dispersity of galena on the amount of solid phase in the foam. (Dispersity in sieve meshes per square centimeter.)

optimum concentration is approximately 0.000025 molar for particles varying in size between 4500 and 9000 sieve-meshes per square centimeter while for particles which pass a 12,000-mesh sieve there is a marked increase in the optimum concentration of oleic acid which is not accompanied by anything like a corresponding increase in the weight of material going into the foam. Thus, we see that if the particles are too large, the force of gravity carries them down out of the foam whereas, if they are too minute, the weight required to cover a given oleic acid film is

too small. In flotation practice, therefore, the particles of ore must be fine but not too fine or the amount of oil required will be unnecessarily large.

MECHANISM OF FROTH FLOTATION

The mechanism whereby the sulfide particles concentrate in the foam is that of selective adsorption. The sulfide particles adsorb the collector and are carried into the interface, whereas the gangue material does not adsorb the collector and so is not carried up into the froth. This is illustrated in a striking way by some observations of Bartsch¹ on the relative adsorption of oleic acid by equal volumes of the various minerals (Table XXIII). The relative concentrations of oleic acid before and after shaking with the mineral are expressed as the "drop num-

TABLE XXIII.—ADSORPTION OF OLEIC ACID BY MINERALS

Minerals	Drop number after adsorption from 20 cubic centimeters of acid				
	0.001	0.002	0.003	0.003	0.0002
Concentration of oleic acid, molar.					
Drop number before ad- sorption.	68.8	73.4	78.4	78.4	48.0
Chalcopyrite.....	38.0	42.9	40.2	49.5	38.6
Molybdenite.....	38.0	55.3	48.0	52.2	43.5
Galena.....	37.9	47.5	48.2	53.0	39.5
Zinc blende.....	40.0	56.9	53.4	53.3	42.5
Pyrites.....	53.2	57.8	58.4	56.4	42.9
Feldspar.....	66.7	71.2	76.3	76.7	
Quartz.....	68.2	72.9	77.2	77.3	
Dispersity of minerals, sieve-meshes per square centimeter.	4,000 to 9,000	900 to 1,500	1,500 to 4,000	900 to 1,500	1,500 to 4,000

¹ *Kolloidchem. Beihefte*, **20**, 68 (1925); cf. TRAUBE and NISHIZAWA; *Kolloid-Z.*, **32**, 383 (1923); cf. TAGGART and GAUDIN: *Trans. Am. Inst. Mining Met. Eng.*, **68**, 479 (1923).

ber."¹ The values were obtained by neutralizing the suspended oil with alkali and measuring with a stalagmometer the number of drops in a given volume of the resulting soap solutions. It will be noted that the drop number of the several solutions is reduced but slightly by shaking with feldspar or quartz, showing that this gangue material does not adsorb oleic acid appreciably. The sulfide ores, on the other hand, are adsorbed quite strongly by the sulfide minerals in the approximate order; chalcopyrite > molybdenite, galena > zinc blende > pyrites.

The difference in the tendency of the sulfide ores to concentrate in the foam under varying experimental conditions lies at the basis of the differential or preferential flotation of the sulfide ores.¹ In practice, the flotation of zinc ores is facilitated by the addition of a small amount of copper salt. This is probably due to the coating of the zinc sulfide particles with a film of copper sulfide which is more readily floated. On the other hand, the floating of zinc sulfide is hindered by the addition of such salts as the sulfates of magnesium, sodium, potassium, manganese, zinc, and iron, and the cyanides of sodium and zinc, thereby making it possible to separate galena from sphalerite² technically.

Attention should be called to Edser's³ view that the role of the oleic acid or kerosene is to enlarge the contact angle between the air-liquid surface and the water-solid interface of the sulfide. It appears, however, that oil acts by being adsorbed by the particles rather than by changing an alleged contact angle. Thus Vageler⁴ found that certain oxide ores show the same contact angle as the gangue; and yet the ores adsorb oleic acid quite strongly and can be floated⁵ whereas the gangue does not adsorb oleic acid and is not floated (see Table XXIV).⁶

¹ For details see RALSTON: Rickard's "Concentration by Flotation," 378-401; FREEMAN: *Ibid.*, 657, 663 (1921).

² LYSTER: British Patent, 11939 (1913); U. S. Patent, 1203372 (1916); cf. GREENWAY and LOWRY: British Patent, 11471 (1913); U. S. Patent, 1102738 (1914).

³ "Brit. Assocn. Advancement Sci., Fourth Rept. on Colloid Chemistry," 267 (1922).

⁴ "Die Schwimmaufbereitung der Erze," Dresden (1921).

⁵ Cf. BERL and PFANNMÜLLER: *Kolloid-Z.*, 35, 34 (1924).

⁶ BARTSCH: *Kolloidchem. Beihefte*, 20, 72 (1925).

TABLE XXIV.—ADSORPTION OF OLEIC ACID BY OXIDIC MINERALS

Adsorbent	Drop number of 0.002 molar oleic acid		Remarks
	Before adsorption	After adsorption from 20 cubic centimeters of acid	
Alumina.....	73.4	51.0	Will float
Iron oxide.....	73.4	42.0	Will float
Siderite.....	73.4	49.5	Will float
Heavy spar.....	73.4	46.2	Will float
Feldspar.....	73.4	71.2	Will not float
Quartz.....	73.4	72.9	Will not float

Action of Acids.—In flotation practice it has been found that a better separation of sulfides, especially zinc sulfide, from the gangue is obtained in slightly acid rather than neutral solution. This is readily understood in the light of Bartsch's¹ observations of the action of acid on the adsorption of oleic acid by the sulfide minerals and gangue (Table XXV). The decrease in the drop number in the presence of sulfuric acid is evidence of a stronger adsorption of oleic acid by the mineral and hence of a greater

TABLE XXV.—EFFECT OF SULFURIC ACID ON THE ADSORPTION OF OLEIC ACID BY MINERALS

Mineral	Drop number after adsorption from 20 cubic centimeters of 0.002 molar oleic acid	
	Without H ₂ SO ₄	With 0.001 N H ₂ SO ₄
Chalcopyrite.....	42.9	38.7
Molybdenite.....	55.3	40.2
Galena.....	47.5	38.3
Zinc blende.....	56.9	39.2
Pyrites.....	57.8	47.0
Quartz.....	71.2	71.4
Feldspar.....	72.2	72.6

¹ *Kolloidchem. Beihefte*, 20, 70 (1925).

tendency to float. This effect is most marked for zinc blende. The adsorption by the gangue material is negligible in both the neutral and acid media. The greater adsorption by the sulfides in the presence of acid is probably due in large part to its cleansing action on the surface of the particles.

Action of Protective Colloids.—Protective colloids such as gelatin, saponin, and soap cut down the amount of ore which concentrates in the foam as shown in Table XXVI,¹ in spite of the fact that such agents increase the frothing enormously. Bartsch² has shown that the protective colloids are strongly adsorbed by the sulfide particles; this cuts down the adsorption of a collector such as oleic acid and so decreases the amount which goes into the foam. Since the action is specific, different ores

TABLE XXVI.—EFFECT OF PROTECTIVE COLLOIDS ON ORE FLOTATION
(Oleic acid concentration 0.00005 molar. Isoamyl alcohol concentration
0.25 per cent)

Ores, 13 grams	Grams solid phase in the foam after addition of			
	Saponin, 0.000 per cent	Saponin, 0.001 per cent	Saponin, 0.004 per cent	Saponin, 0.008 per cent
Zinc blende.....	9.23	9.81	9.63	7.03
Galena.....	8.34	5.85	1.07	0.20
Chalcopyrite.....	7.35	7.05	2.98	0.49
Pyrites.....	2.34	0.32	0.03
Molybdenite.....	2.54	2.66	0.25	0.02

Ores, 13 grams	Gelatin, 0.000 per cent	Gelatin, 0.0001 per cent	Gelatin, 0.001 per cent	Gelatin, 0.003 per cent
Zinc blende.....	9.23	9.98	9.84	6.31
Galena.....	8.34	8.41	8.33	1.72
Chalcopyrite.....	7.35	7.45	6.35	1.45
Pyrites.....	2.34	1.62	1.13	
Molybdenite.....	2.54	2.65	2.36	0.26

¹ BARTSCH: *Kolloidchem. Beihefte*, **20**, 42 (1925).

² *Kolloidchem. Beihefte*, **20**, 71 (1925).

behave differently in the presence of the same protective colloid. Thus the concentration of zinc blende in the foam is decreased but slightly in the presence of quantities of saponin or gelatin, which will eliminate most of the other sulfides from the foam.

CLASSIFICATION

In the froth-flotation process patented originally by the Minerals Separation Company,¹ the relative amounts of air, oil, and pulverized ore are such that the bubbles of froth are armor plated and are therefore relatively stable. If the amount of air is excessive relatively to the ore, the bubbles are not completely coated and are therefore instable. These bubbles float up the ore but they break shortly after reaching the surface, releasing the ore particles which must be removed before they settle back with the gangue. This principle is involved in Callow's flotation process.² There are, therefore, two general types of froth-flotation processes. To quote from Taggart:³

Froth flotation comprises two entirely different types of processes which resemble each other only in the fact that in both the concentrate is removed in the form of a froth composed of gas, liquid, and solid matter, preponderantly sulfide material. The processes differ fundamentally both in the place in which concentration is done and in the mechanism of the selection of sulfide from gangue. On the basis of the first difference the processes may be classified as pulp-body-concentration processes and bubble-column-concentration processes.

Pulp-body-concentration processes may be subdivided, on a basis of introducing bubble-making gas, into four types: (1) chemical-generation, (2) pressure-reduction, (3) boiling, and (4) agitation. All four types depend upon the fact that in a pulp, the liquid part of which is saturated with a gas, preferential precipitation of the gas on the sulfide particles can be brought about by so changing the conditions of the temperature and pressure that the liquid is, under the changed conditions, supersaturated. This preferential precipitation of gas from the supersaturated liquid is enhanced, if the sulfide particles are coated with an oil substance, and the presence of such a substance always makes greater the force of adherence between the precipitated bubbles and sulfide

¹ SULMAN, PICARD, and BALLOT: British Patent, 7803; U. S. Patent, 835120 (1905).

² CALLOW: U. S. Patent, 1104755 (1914).

³ "A Manual of Flotation Processes," 3 (1921).

particles. As the result of this preferential precipitation of gas on sulfide particles in the pulp, and its adhesion thereto, there are formed in the body of the pulp agglomerates consisting of one or more gas bubbles with sulfide particles firmly cemented to them. These agglomerates later rise to the surface in the form of a froth which is separated as concentrate. Observation of any of the pulp-body-concentration processes shows clearly this phenomenon of rising agglomerates whose color indicates distinctly that concentration has been completed at the surfaces of the bubbles composing them *below the surface of the pulp*, that is, within the pulp body . . .

The froth produced in the pulp-body-concentration processes are small bubbles, coherent and persistent, and characteristic. The volume of gas effectively utilized in floating the mineral is of the order 20 to 50 cubic feet of solid floated.

In the bubble-column process, substantially all the concentration is done in a column of bubbles above and floating on the surface of the body of pulp. In this process the volume of gas effectively used to produce concentration is enormously greater than in pulp-body concentration, being of the order of 1000 to 2000 cubic feet of solid floated. The result is that the froth is gradual and evanescent and strikingly different from the characteristic of the other class of processes. Further investigation of the process, by observation of the operation in the glass-sided machines, makes apparent the following facts: (1) the bubbles are much larger than in pulp-body-processes; (2) they are more numerous; (3) they rise from the pulp more rapidly; (4) they arrive at the surface of the pulp with a solid load composed of sulfide and gangue in the same proportions that these exist in the pulp through which they have passed; (5) concentration begins at the bottom of the bubble column (*i.e.*, the surface of the pulp body) and progresses upward. The actual mechanism of the concentration itself can be observed by studying the bubble column with a hand glass. Such study shows that in the bubble walls there is a differential draining of the gangue and sulfide particles; that the average downward velocity of the sulfide particles is less than the average upward velocity of the bubbles; that the average downward velocity of the gangue is greater than the average upward velocity of the bubbles; and that, as a result, the sulfides are lifted up and away from the gangue. It is apparent, also, from such study that the sulfide particles in the bubble column are nowhere firmly adherent to the bubbles, as they are in the pulp-body processes.

THE AGGLOMERATION PROCESS

The agglomeration process of ore concentration invented by Cattermole in 1903 is not a flotation process but it depends on the

selective adsorption of oil by sulfide ores and so should be mentioned. In this process, a quantity of oil is added to a flowing pulp in the absence of air bubbles. Under these conditions, the sulfide particles agglomerate into large globules or granules which are heavier than the gangue and so sink to the bottom, allowing the gangue to be washed away. While the principle is sound, technical processes using it never proved to be sufficiently successful to compete with froth-flotation processes.¹

¹ HEBBARD: Rickard's "Concentration by Flotation," 199 (1921).

CHAPTER X

THE PHOSPHORESCENT SULFIDES AS COLLOID SYSTEMS

When properly prepared, certain sulfides have the property of phosphorescing after exposure to sunlight or artificial light of short wave length. This phenomenon was first observed in 1602 by Casciorolus, a Bolognese shoemaker, with a barium sulfide obtained by calcining barium with carbon. Margraff likewise obtained a luminescent calcium sulfide by calcining gypsum with combustible matter; and Canton¹ prepared a similar compound by calcining oyster shells and sulfur. Phosphorescent zinc sulfide was first prepared by Sidot² by heating zinc blende in a stream of sulfur dioxide, hydrogen sulfide, and nitrogen. The phosphorescent sulfides of barium, calcium, and zinc are frequently referred to as Bolognian phosphor, Canton's phosphor, and Sidot's blende, respectively. It is of particular interest that the chemically pure sulfides are not phosphorescent on exposure to sunlight but a trace of some heavy metal such as copper, bismuth, or manganese must be present. Moreover, there appear to be centers of phosphorescence containing the heavy metals and the quality of the phosphorescent light is dependent to a large extent on the nature of the impurity. This suggests that the phosphorescent sulfides or phosphors, as they are called, should be regarded as colloid systems.

FORMATION AND PROPERTIES

Until the early years of the present century, the phosphorescent bodies were obtained more or less accidentally. Thus, Vanino and Zumbusch³ heated alkaline earth oxides, carbonates, or

¹ *Phil. Trans.*, **58**, 337 (1768).

² *Compt. rend.*, **63**, 188 (1866).

³ *J. prakt. Chem.*, [2] **80**, 69 (1909); **82**, 193 (1910); **84**, 305 (1911); VANINO and GANS: *Ibid.*, **71**, 196 (1905).

hydroxides with sulfur, obtaining sulfides, the phosphorescence of which was attributed to the presence of a small amount of polysulfide. Similarly Verneuil¹ obtained phosphorescent zinc sulfide by heating natural blende or the precipitated sulfide in a stream of hydrogen or hydrogen sulfide. Henry² heated to a white heat the sulfide precipitated with hydrogen sulfide from an ammoniacal zinc chloride solution and Arnold³ heated: (1) zinc with cinnabar, (2) zinc oxide in hydrogen sulfide, (3) zinc sulfate with sulfur and carbon, and (4) zinc sulfide from ammoniacal zinc chloride. Such directions give but little indication of the essential conditions for forming a phosphorescent body; but as a result of extended investigations, especially by Lenard and his collaborators,⁴ the experimental conditions which yield phosphors are now quite well defined. To prepare a phosphor, three essential components must be thoroughly mixed and heated to a high temperature: (1) the sulfide, (2) a small amount of heavy metal which will yield a colored sulfide, and (3) a colorless flux. A convenient procedure consists in adding the trace of heavy metal salt to the zinc salt solution before precipitation. The gel is then washed and dried, mixed with the flux, and ignited.

The Sulfide.—As already noted, the sulfides of calcium, strontium, barium, and zinc are the basis of the most important sulfide phosphors. Phosphorescent sulfides of beryllium⁵ and magnesium⁶ and of sodium and rubidium⁷ have also been obtained. One seems justified in concluding, therefore, that all of the white sulfides of the first and second groups may be the basis of phosphors.

The Heavy Metal Impurity.—Some of the early investigators⁸ believed that a very pure sulfide was essential for marked phosphorescence. It has been demonstrated repeatedly, how-

¹ *Compt. rend.*, **106**, 1104; **107**, 101 (1888).

² *Compt. rend.*, **115**, 505 (1892).

³ *Wied. Ann.*, **61**, 315 (1897).

⁴ KLATT and LENARD: *Wied. Ann.*, **38**, 90 (1889); *Ann. Physik*, [4] **15**, 225, 633 (1904); LENARD: *Ibid.*, **31**, 675 (1910).

⁵ BILTZ: *Z. anorg. Chem.*, **82**, 438 (1913).

⁶ TIEDE: *Ber.*, **49**, 1745 (1916); TIEDE and SCHLEEDE: *Ber.*, **53**, 1721 (1920); *Ann. Physik*, [4] **67**, 573 (1922); TIEDE and RICHTER: *Ber.*, **55 B**, 69 (1922).

⁷ TIEDE and REINICKE: *Ber.*, **56 B**, 666 (1923).

⁸ Cf. VERNEUIL: *Compt. rend.*, **106**, 1104; **107**, 101 (1888).

ever, that chemically pure salts¹ are incapable of phosphorescence, the phenomenon taking place only when the zinc² or alkaline earth³ sulfide is contaminated with a trace of heavy metal impurity. The active impurity is sometimes referred to as the exciter. The amount required to bring about phosphorescence is so small relatively that special precautions must be observed in preparing a chemically pure non-phosphorescent sulfide as standard. Tomaschek⁴ used the following procedure in preparing a pure zinc sulfide: A 10 per cent solution of zinc sulfate was acidified with nitric acid and treated with hydrogen sulfide until it was cloudy. The solution was filtered through a membrane filter, treated with more nitric acid and boiled for some time, after which it was neutralized with ammonia to incipient precipitation and the dirty precipitate filtered off. The clear solution was next made slightly acid with sulfuric acid and electrolyzed warm, air being bubbled through the solution at the same time. After filtering, the filtrate was treated with an excess of ammonia and saturated with hydrogen sulfide. The precipitate was washed thoroughly with hot water, dried, and ignited. Schleede and Gantzkow⁵ obtained a non-phosphorescent salt from a dilute solution of recrystallized zinc sulfate which was made slightly alkaline with specially prepared ammonia⁶ and precipitated with specially prepared hydrogen sulfide.⁷

Starting with a pure sulfide, Tomaschek showed that the presence of as little as 0.000006 gram Cu per gram ZnS is sufficient to induce a bright phosphorescence. Increasing the heavy metal content increases the intensity of the momentary luminescence⁸

¹ LEBON: *Rev. sci.*, II, 338 (1900); DE VISSER: *Rec. trav. chim.*, **20**, 435 (1901).

² HOFMANN and DUCCA: *Ber.*, **37**, 3407 (1904); GRÜNE: *Ibid.*, **37**, 3076 (1904); JORISSEN and RINGER: *Ibid.*, **37**, 3983 (1904).

³ LENARD and KLATT: *Ann. Physik*, [4] **15**, 225, 425, 633 (1904); VANINO and GANS: *J. prakt. Chem.*, [2] **71**, 196 (1905); MOURELO: *Compt. rend.*, **129**, 1236 (1899); **160**, 174; **161**, 172 (1915); WAENTIG: *Z. physik. Chem.*, **51**, 435 (1905); BURNINGHAUS: *Compt. rend.*, **144**, 839, 1040 (1907); KOWALSKY and GARNIER: *Ibid.*, **145**, 391 (1907).

⁴ *Ann. Physik*, [4] **65**, 189 (1921).

⁵ *Z. physik. Chem.*, **106**, 37 (1923).

⁶ RICHARDS, KÖTHNER, and TIEDE: *Z. anorg. Chem.*, **61**, 323 (1909).

⁷ TIEDE and SCHLEEDE: *Ber.*, **53**, 1721 (1920).

⁸ See p. 166.

up to a certain point and then causes it to decrease.¹ For a zinc-copper phosphor, the maximum concentration is 0.0002 gram Cu per gram of ZnS and for a zinc-manganese phosphor it is 0.004 gram Mn per gram of ZnS.²

Failure to start with pure material and to recognize the importance of the right amount of impurity, are responsible for a great many contradictory observations. Thus MacDougall, Stewart, and Wright³ claim that most of the elements of the periodic table will cause zinc sulfide to give a green phosphorescence when isolated. This observation is undoubtedly due to the presence of a trace of copper in the original sulfide. Similarly, Schmidt⁴ claims that the phosphorescence of zinc sulfide is weakened or actually prevented by the presence of salts which give dark-colored or black sulfides and so recommends the use of sodium tungstate as an exciter. It is altogether probable that Schmidt's preparation contained copper to start with: first, because he did not take special precautions to remove it, and second, because his product gave what he called "magic green" phosphorescence which is characteristic of the zinc-copper phosphor. When he added copper he exceeded the maximum amount for good phosphorescence and so came to the erroneous conclusion that copper and similar metals must be avoided in preparing zinc phosphors.⁵

Iron salts are said to have a destructive effect on the glow of zinc sulfide⁶ but this, too, appears to be a conclusion based on faulty experimentation, since Schleede and Gantzekow⁷ find iron salts to be effective in amounts but one-fifth that of copper. Since copper and manganese are especially good excitors for both zinc sulfide and the alkaline earth sulfides and since iron is a good exciter for the latter, it is not surprising to find that it works with the former when present in the right amount. It is not always true, however, that a good exciter for one phosphor will be a good exciter for another phosphor. Thus the presence of a trace of

¹ Cf., also, LENARD and KLATT: *Ann. Physik*, [4] **15**, 225, 425, 633 (1904).

² TOMASCHEK: *Ann. Physik*, [4] **65**, 189 (1921).

³ *J. Chem. Soc.*, **111**, 663 (1917).

⁴ *Ber.*, **55B**, 3988 (1922).

⁵ Cf. TIEDE and SCHLEEDE: *Ber.*, **56B**, 674 (1923).

⁶ MACDOUGALL, STEWART, and WRIGHT: *J. Chem. Soc.*, **111**, 663 (1917).

⁷ *Z. physik. Chem.*, **106**, 37 (1923).

bismuth salts will cause the alkaline earth sulfides to phosphoresce brightly, whereas zinc-bismuth phosphors glow but faintly at ordinary temperatures.¹

Observations on the effect of cadmium on a zinc-sulfide phosphor are conflicting. Thus Tiede and Schleede² obtained a good phosphor containing 0.0001 gram of cadmium per gram of zinc sulfide, whereas Guntz³ found that the presence of 1 per cent of cadmium sulfide is without effect, although greater amounts give a phosphor which glows citron yellow with 12 per cent cadmium sulfide, orange with 20 per cent cadmium sulfide, and red with 30 per cent cadmium sulfide.

The Flux.—The presence of one or more alkali or alkaline earth salts in amounts up to 10 per cent favor the formation of a phosphor with a long period of phosphorescence.⁴ Vanino and Zumbusch⁵ observed that sodium sulfate (melting point 880°) and lithium carbonate (melting point 660°) have a greater effect than potassium sulfate (melting point 1074°) in increasing the phosphorescence and that, as a rule, salts of a low melting point have more influence than those of a high melting point. Alkali chlorides have usually been recommended for the flux in preparing zinc-sulfide phosphors, but Tomaschek found that alkali fluorides and mixed alkali and alkaline earth fluorides give as good or better results.

While the presence of a flux is desirable in preparing phosphors, it is not essential, as sometimes supposed. Tiede and Schleede⁶ heated both alkaline earth sulfides and zinc sulfides to a temperature sufficiently high to cause sintering or melting in the absence of a flux, and obtained good phosphors. Since pure zinc sulfide vaporizes below its melting point the required temperature was realized by heating under 100 atmospheres pressure. The purpose of the flux is to get a satisfactory crystalline structure at a moderate temperature. That it plays but an intermediate role is evidenced by the fact that a soluble flux can

¹ TOMASCHEK: *Ann. Physik*, [4] **65**, 189 (1921).

² *Ber.*, **53**, 1721 (1920).

³ *Compt. rend.*, **177**, 479 (1923).

⁴ LENARD and KLATT: *Ann. Physik*, [4] **15**, 225, 663 (1904).

⁵ *J. prakt. Chem.*, [2] **80**, 69 (1909); **82**, 193 (1910).

⁶ *Ber.*, **53**, 1721 (1920); *Centr. Mineral. Geol.*, **154** (1921).

be washed out quantitatively after ignition without influencing the phosphorescence appreciably.

To obtain a good zinc-copper phosphor Tomaschek¹ found the optimum ignition temperature with a flux to be 950 to 1000° and for a zinc-manganese phosphor, 1100°. Prolonged phosphorescence is favored by ignition for a considerable time; but 30 minutes is usually sufficient to give a satisfactory product. The actual temperature and time of ignition necessary to get a product possessing the required structure will naturally vary with different sulfides.

Crystal Structure.—A sulfide will not phosphoresce unless it possesses a distinctly crystalline structure.² If the ignition temperature is so high that the surface of the sulfide is glazed no phosphorescence will result.³ Schleede⁴ claims that sudden cooling of the ignited sulfide causes crystal deformation which is essential for a good phosphor. Phosphorescence can be entirely prevented in a zinc sulfide containing the required ingredients, by allowing the crystals to form slowly and uniformly.⁵ An x-radiogram of a highly phosphorescent zinc sulfide gives evidence of crystal deformation.⁶

While the alkaline earth sulfides crystallize in the cubic system only, zinc sulfide crystallizes as both blende and wurtzite, the transition point being 1020°. Some evidence indicates that both forms can be made phosphorescent⁷ but Schleede claims that the property is associated with wurtzite alone. In support of this view is Tomaschek's observation that the best phosphors are obtained by ignition at a high temperature and Guntz's⁸ report that wurtzite phosphors glow longer than blende phosphors. The weaker phosphorescence of the latter is attributed by Schleede to the presence of a small amount of wurtzite in the

¹ *Ann. Physik*, [4] **65**, 189 (1921).

² SCHLEEDE and GANTZCKOW: *Z. physik. Chem.*, **106**, 46 (1923).

³ LENARD: *Heidelberger Ber.* (1918); SCHLEEDE and GANTZCKOW: *loc. cit.*

⁴ *Z. Physik*, **18**, 109 (1923).

⁵ TIEDE and SCHLEEDE: *Ber.*, **53**, 1721 (1920).

⁶ SCHLEEDE and GANTZCKOW: *Z. physik. Chem.*, **106**, 37 (1923).

⁷ GUNTZ: *Compt. rend.*, **174**, 1356 (1922); **177**, 479 (1923); TOMASCHEK: *Ann. Physik*, [4] **65**, 189 (1921).

⁸ *Compt. rend.*, **174**, 1356 (1922); **177**, 479 (1923).

blende rather than to the blende itself. In line with this Schleede and Gantzkow found by x-ray analysis that wurtzite is converted into blende by grinding; and grinding a zinc sulfide phosphor destroys its power to phosphoresce.¹ On the other hand, grinding or applying pressure to an alkaline earth phosphor likewise destroys its phosphorescing power without any change in the crystal structure.²

The phosphors may be almost white in color but as a rule they are darkened somewhat by the presence of the heavy metal sulfide. Zinc sulfide phosphors are blackened by exposure to light³ owing to the liberation of metallic zinc. The prolonged action of light causes an appreciable decrease in the intensity of the phosphorescence. Thus, 300 hours' exposure to a mercury lamp cuts down the intensity to three-fourths the original value.⁴ The reducing action of formaldehyde is much more pronounced, 15 minutes in the vapors of the compound reducing the intensity 95 per cent.⁵ Since, in both cases, the surface of decomposition is covered with finely divided zinc, it is probable that the black film of metal is largely responsible for the diminished intensity of the glow.

Grinding or the application of pressure to both alkaline earth and zinc phosphors causes all of them to change color on subsequent exposure to light.⁶ The original color is restored by warming or by the action of red light. The cause of the discoloration after pressure is uncertain. The phenomenon reminds one of the photochemical decomposition of zinc sulfide but just how the application of pressure would bring about the decomposition of an alkaline earth phosphor is not obvious.⁷

¹ GUNTZ: *Compt. rend.*, **174**, 1356 (1922); MAASS and KEMPF: *Z. angew. Chem.*, **36**, 296 (1923).

² LENARD and KLATT: *Ann. Physik*, [4] **12**, 439 (1903); LENARD: *Elster-Geitel Festschrift*, 669 (1915); *Ann. Physik*, [4] **68**, 563 (1922).

³ LENARD: *Ann. Physik*, [4] **31**, 652 (1910).

⁴ LOEB and SCHMIEDESKAMP: *Proc. Nat. Acad. Sci.*, **7**, 202 (1921); BAERWALD: *Ann. Physik*, [4] **39**, 849 (1912).

⁵ LENARD: *Ann. Physik*, [4] **68**, 569 (1922).

⁶ LENARD and HAUSSER: *Heidelberger Ber.*, 19th paper (1913); LENARD: *Elster-Geitel Festschrift*, 669 (1915).

⁷ Cf. STALONY-DOBROZAŃSKI: *Z. Physik*, **38**, 841 (1926).

The action of light on a phosphor in many instances increases the conductivity of the powder.¹ Light also increases the dielectric constant of phosphorescent sulfides, especially Sidot's blende.² It has been suggested that the strongly marked crystalline structure of zinc sulfide is an important factor in the latter phenomenon, and that the effect may be connected with the selective photoelectric effect of copper, which is the active material in phosphorescent blende.

THE PHOSPHORESCENT LIGHT

The phosphorescence spectrum always consists of one or more continuous bands having maxima at different wave lengths, the position and number of which depend on the nature of the sulfide and the small amount of heavy metal impurity. The intensity and duration of the luminescence is influenced by the wave length of the exciting light, the temperature of the phosphor, and, as already noted, by the flux employed and the ignition temperature. These several effects are illustrated by some observations of Tomaschek on zinc sulfide phosphors as given in Table XXVII.

TABLE XXVII.—ZINC SULFIDE PHOSPHORS

Heavy metal, grams per gram of ZnS	Flux	Ignition		Color of phosphorescence	
		Time, minutes	Temper- ature, degrees centigrade	Room temperature	After exciting at -180° and warming
Cu 0.0001.....	NaCl + MgF ₂	100	1000	Bright green	
Mn 0.0020.....	CaF ₂ + KCl	30	1300	Lasting, clear yellow red	
Bi 0.0040.....	Na ₂ SO ₄ + CaF ₂	30	900	Weak dark red	Clear blue to strong red
Pb 0.0002.....	K ₂ SO ₄	15	900	Very weak	Very clear blue to yel- low green
Ag 0.0002.....	CaF ₂ + KCl	30	900	Very weak	Clear violet
Ur 0.0010.....	None	Yellow

¹ GUDDEN and POHL: *Z. physik*, **1**, 365 (1920); **2**, 181, 361 (1920); **4**, 206 (1921); **7**, 65 (1921); *Ann. Physik*, [4] **68**, 154 (1922); MOLTHAN: *Z. physik*, **4**, 262 (1921); TOMASCHEK: *Ann. Physik*, [4] **65**, 189 (1921); CURIE: *Compt. rend.*, **172**, 272 (1921); RUPP: *Ann. Physik*, [4] **72**, 81 (1923).

² GUDDEN and POHL: *Ann. Physik*, [4] **68**, 154 (1922); HERWEG: *Z. physik*, **16**, 23 (1923); SCHMIDT: *Ann. Physik*, [4] **64**, 722 (1921).

The conditions noted are those which give the best phosphor with the several heavy metal impurities. The aluminum spark was used as the exciting light.¹

For any given phosphorescence band in the spectrum, there are usually three or more exciting bands whose wave lengths are

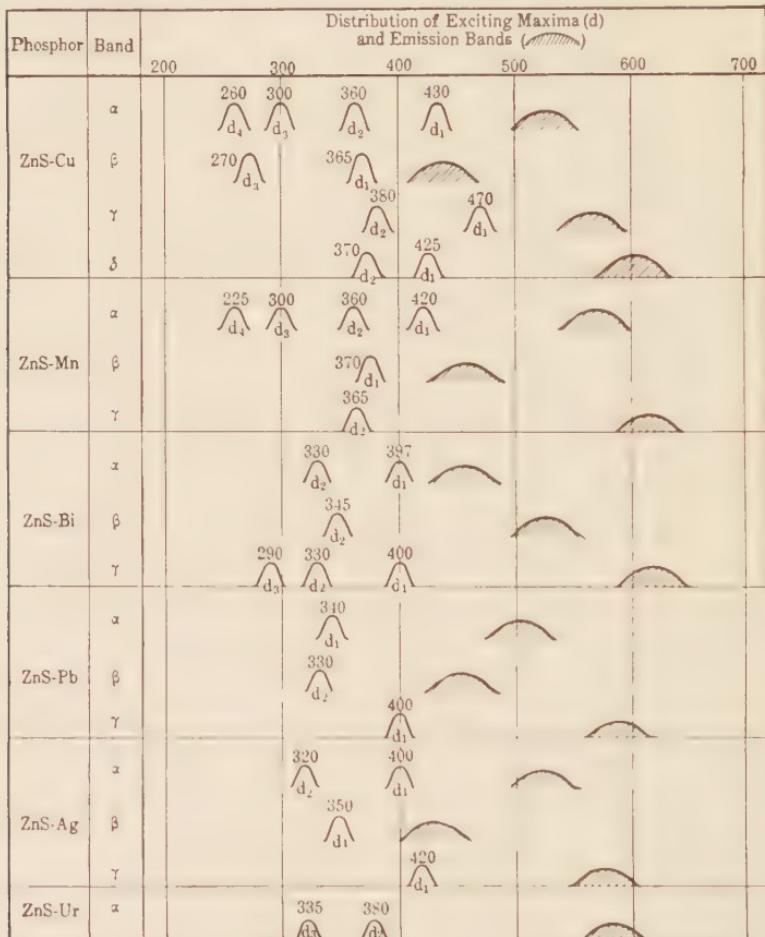


FIG. 16.—Distribution of exciting bands and phosphorescence bands in zinc sulfide phosphors.

shorter than the emission band, in accord with Stokes' law. In Fig. 16 is shown the position of the several exciting bands and of the phosphorescence bands for the zinc sulfide phosphors referred to in Table XXVII on page 163.

¹ SCHMIDT: *Ann. Physik*, [4] 63, 273 (1920).

The different luminescent bands have their maxima at different temperatures. Thus, the optimum emission temperature of the green α band of the zinc-copper phosphor is at 20° while the violet β band and the reddish-yellow γ are cold bands, having their optimum emission at -60 and -100° , respectively. The yellow γ band phosphoresces from -180 to $+130^\circ$ but the glow is of short duration at room temperature. The effect of temperature on the color of phosphorescence is shown in striking fashion with strontium sulfide, which glows pale violet at -20° , violet blue at 20° , pale blue at 40° , green at 70° , yellow at 100° , and pale orange at 200° .¹

Since every band of the phosphorescence spectrum has a definite temperature range, it cannot be generally true as older observers² believed, that warming an excited phosphor always increases the intensity of the glow and cuts down the time of glow. Thus, Nichols and Merritt³ measured the time of decay of the phosphorescence of a zinc sulfide phosphor between -125 and 200° , finding one temperature of maximum duration of glow at 20° , a second at -40° , and a third at -160° . In general, however, an excited phosphor which has ceased to glow at room temperature will exhibit thermo-luminescence for a short time on warming suddenly.⁴ All phosphors may be excited at so low a temperature that they exhibit no phosphorescence whatsoever but they will start to glow on warming to a temperature corresponding to the optimum for one of the emission bands. The glow is usually eliminated or of short duration at high temperatures; thus, zinc sulfide phosphors cease to phosphoresce above 200° .⁵

At some one temperature a given band may be produced by different processes distinguished by the duration of the luminescence and the wave length of the exciting rays. Thus, if the exciting spectrum falls on the phosphor a few seconds only,

¹ BECQUEREL: *Compt. rend.*, **104**, 551 (1887); cf. MOURELO: *Ibid.*, **160**, 174 (1915).

² DREHER: *Chem. Ztg.*, **5**, 726 (1881); PICTET and ATSCHUL: *Z. physik. Chem.*, **15**, 386 (1894); LE ROUX: *Compt. rend.*, **140**, 84, 239 (1905).

³ *Phys. Rev.*, **32**, 38 (1911).

⁴ VANINO and ZUMBUSCH: *J. prakt. Chem.*, [2] **80**, 69 (1909); DALMS: *Ann. Physik*, [4] **13**, 438 (1904); LE BON: *Rev. Sci.*, II, 296 (1900).

⁵ WIEDEMANN and SCHMIDT: *Wied. Ann.*, **56**, 219 (1895).

certain parts of the surface light up at once but cease to glow as soon as the exciting light is removed. This "momentary process" corresponds to fluorescence. If the excitation is continued for some time, the glow increases to a maximum and continues after the exciting rays are cut off. This is the "phosphorescence process." Although the exciting regions or bands for the two processes usually overlap, they are never coincident. As we have seen, there are usually three or more fairly sharp exciting bands for the phosphorescence process while for the momentary process there is but one band, broader and less sharply defined. In many instances, there is a third process which Lenard¹ calls the "ultraviolet process." This manifests itself by a relatively faint glow when the sulfide is exposed to the extreme ultraviolet. The luminescence bands apparently have the same location in the spectrum for each of the three processes. It is interesting to note that Stokes' rule does not hold absolutely for all phosphors. Thus for the α band of the zinc-copper phosphor, Gudden² finds the shortest wave length of the emission to be $470\mu\mu$ where that of the exciting light is $497\mu\mu$.

A sulfide phosphor may be saturated by excitation so that further action of light has no effect on the intensity of the glow³. Observations on the decay of an excited phosphor disclose that the "light sum," that is, the integrated phosphorescence emission up to the time when the glow ceases, is independent of the temperature, being the same whether the process takes place slowly at a low temperature, more rapidly at an elevated temperature, or partly at one temperature and partly at another. If instead of heat, infra-red rays are used to speed up the process, the light sum is diminished.⁴ The first effect of the excitation is usually a sudden increase in brightness, but this is not always true.⁵

¹ *Ann. Physik*, [4] **31**, 645 (1910).

² *Physik. Z.*, **24**, 465 (1923).

³ LENARD: *Heidelberger Ber.*, **43** (1912).

⁴ WIEDEMANN and SCHMIDT: *Wied. Ann.*, **56**, 219 (1895); MOURELO: *Compt. rend.*, **128**, 557 (1899); HOFMANN and DUCCA: *Ber.*, **37**, 3407 (1904); NICHOLS and MERRITT: *Phys. Rev.*, **21**, 247 (1905); CURIE: *Compt. rend.*, **172**, 272 (1921); **173**, 554; **174**, 550 (1922).

⁵ ARNOLD: *Wied. Ann.*, **61**, 314 (1897); IVES and LUCKIESH: *Astrophys. J.*, **34**, 173 (1911); **36**, 330 (1912); *Phys. Rev.*, **34**, 156 (1912); TAYLOR: *J. Phys. Chem.*, **31**, 115 (1927).

The effects are similar to those produced by heating, although the actual elevation of temperature of the phosphor is slight. To get around this difficulty, Lenard¹ assumes that the infrared radiation causes a local heating of the "centers" of emission.

Using a photoelectric method, Lenard and Hausser² followed the decay of phosphorescence on a large number of phosphors. Some observations on the α band of a zinc-copper phosphor excited by a mercury lamp are given in Table XXVIII. The numbers in the column headed "light sum" were read off the scale of the electrometer and so are arbitrary values.

TABLE XXVIII.—DECAY OF PHOSPHORESCENCE OF THE α BAND IN A ZINC-COPPER PHOSPHOR

Time, minutes	"Light sum"	Time, minutes	"Light sum"
1.0	70.0	26.0	6.8
2.0	57.0	62.0	3.6
5.2	22.8	92.0	1.7
10.0	15.3	125.0	1.2
20.0	10.3		

The law of decay which Lenard and Hausser found to apply in the largest number of cases is that which made $I^{-\frac{1}{2}}$ a linear function of the time (I = intensity of phosphorescence). Actually, this law seldom applies throughout the whole period of decay and does not hold at all in some cases.³

It is of interest to note that the distribution of energy in the luminescence spectrum is the same whether the body is excited by light, by x-rays, by cathode bombardment, or by radioactive radiations. It frequently happens, of course, that the substance tested will not glow under ultraviolet light but will luminesce if excited by more energetic radiation; moreover, the luminescent bands may be excited by the different agencies to a different extent. But if a single band is considered, it will be found that

¹ *Heidelberger Ber.*, Papers 5 and 7 (1917); Papers 8 and 11 (1918).

² *Heidelberger Ber.*, Paper 12 (1912).

³ NICHOLS and MERRITT: *J. Franklin Inst.*, **162**, [2] 226 (1906); *Phys. Rev.*, **21**, 247 (1905); **22**, 279, 287; **23**, 37 (1906); **27**, 367 (1908); **32**, 38 (1911); IVES and LUCKIESH: *Ibid.*, **34**, 156 (1912); *Astrophys. J.*, **34**, 173 (1911); **36**, 334 (1912); PIERCE: *Phys. Rev.*, **30**, 663 (1910); **32**, 115 (1911).

the distribution of energy throughout the band is the same, irrespective of the mode of excitation.¹

MECHANISM OF THE PHOSPHORESCENCE PROCESS

As a result of investigations on the phosphorescence of salts after exposure to cathode rays, Wiedemann and Schmidt² assume that the exciting agent converts the active substance from the stable condition *A* into the unstable condition *B*. If the return of the substance to the condition *A* is accompanied by the emission of light, the phenomenon is called phosphorescence. Thermo-luminescence is accelerated phosphorescence occasioned by increasing the velocity of the phosphorescent reaction by raising the temperature. Fluorescence is attributed either to the change from *A* to *B* or to the fact that the change from *B* to *A* takes place during excitation as well as during the subsequent decay.

Most chemists accept Wiedemann and Schmidt's view that the phosphorescence following excitation of a substance is due to changes which are essentially chemical in nature.³ On the other hand, the majority of physicists⁴ follow Lenard in assuming that the change which Wiedemann and Schmidt referred to as the reaction *A* to *B*, consists in the expulsion of electrons from a molecule of the active substance, while the recombination of the ions formed in this way corresponds to the reverse reaction from *B* to *A*.

Any detailed theory of the mechanism of the action of the sulfide phosphors must account for the important rôle of a trace of heavy metal impurity. The hypothesis first put forward by de Visscher⁵ and Beilby⁶ assumes that the sulfides of zinc, strontium, and barium act as a solvent for the trace of sulfides of copper, manganese, and bismuth which are ionized in the act of forming a solid solution. It is suggested that exposure to

¹ NICHOLS and MERRITT: "Studies in Luminescence," Publication 152, Carnegie Institute of Washington, Chaps. 1 and 9 (1912).

² Wied. Ann., **56**, 243 (1895); WIEDEMANN: *Ibid.*, **37**, 177 (1889).

³ BANCROFT: *J. Franklin Inst.*, **175**, 129 (1913); WILKINSON: *J. Phys. Chem.*, **13**, 691 (1909); TRAUTZ: *Z. physik. Chem.*, **53**, 12 (1908).

⁴ Cf., however, PERRIN: *Ann. phys.*, **11**, 5 (1919).

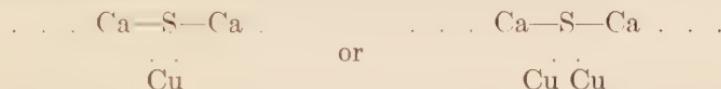
⁵ Rec. trav. chim., **20**, 435 (1901); **22**, 133 (1903).

⁶ Proc. Roy. Soc. (London) **74**, 506 (1905).

light splits the ions still further into electron-like particles which recombine with phosphorescence when the stimulus is removed.

The most widely accepted theory of the structure and action of phosphors is the "center" hypothesis of Lenard. According to this view, light causes one or more electrons to be separated from certain active centers and not uniformly from the entire area of the excited sulfide. The areas from which the electrons are emitted acquire a positive charge while the displaced electrons become attached to sulfur atoms. Phosphorescence is the result of the return of electrons from the sulfur atoms to their original centers.

Instancing the calcium-copper phosphor, Lenard assumes that the center is a complex, $\text{Ca}_x \text{Cu}_y \text{S}_z$, in which the calcium sulfide forms a closed-chain molecule with the added metal forming a kind of side chain that may be represented thus:



The same phosphor may contain a number of different kinds of centers. From such structures, light is supposed to split off from the copper an electron which attaches itself to some neighboring sulfur atom, returning to its former position in the center after a certain interval of time. If the sulfide is too cold during excitation, there is no phosphorescence because the displaced electrons are believed to remain attached. Some, however, do not form such attachments but return at once to produce low-temperature fluorescence. Warming causes the electrons to return to the centers slowly, accompanied by a faint phosphorescence while heating causes a rapid return with a more brilliant glow.¹

The theory of Lenard is usually regarded as fairly satisfactory because it seems to account qualitatively for practically all the phenomena of phosphorescence. Since the same phosphor can contain any number of different kinds of centers, all that one needs to do in order to account for any observed fact is to postulate the existence of a center possessing the necessary properties. While such a flexible theory may possess certain advantages, it must be admitted that it is too indefinite to be regarded as any-

¹ LENARD, ONNES, and PAULI: *Proc. Acad. Sci. Amsterdam*, **12**, 157 (1909).

thing more than a stage in the evolution of a more exact mechanism.

In view of the importance which attaches to the minute amount of impurity in a phosphor, the concept of emission centers containing the impurity would appear to be a distinct contribution to the general theory. Not so much can be said for Lenard's concept of the nature of a center and the way it functions. In the first place, it seems rather far-fetched to assume without any experimental evidence, that the center is a complex chemical combination having such an indefinite composition that it must be represented by such a formula as $\text{Ca}_x \text{Cu}_y \text{S}_z$, to take the case of the calcium-copper phosphor. In the next place, one wonders why it is assumed that light splits off the electrons from copper atoms and the electrons attach themselves to sulfur. In view of the nature of the atoms, the exact reverse is what one would expect to happen. It will be recalled that the action of light on zinc sulfide results in a splitting off from the sulfur of electrons, which becomes attached to the zinc, giving the respective free elements.¹

The Phosphorescent Center.—In the preparation of the sulfide phosphors, relatively large crystals are formed by fusing the amorphous or submicroscopically crystalline mixture of sulfides, usually in the presence of a flux. The minute amount of heavy metal impurity is generally assumed to form a solid solution with the zinc or alkaline earth sulfide, which connotes a more or less uniform distribution of the impurity throughout the entire mass of the phosphor. Since the heavy metal sulfide possesses a crystal lattice different from that of the basic sulfide, it is probable that the crystals of the latter, which grow slowly during the ignition process, will be quite pure, most of the heavy metal impurity being adsorbed at the surface. On account of the very low concentration of heavy metal impurity, the latter will not be distributed over the entire surface but at points or "centers," as it were. From this point of view, a center in a zinc sulfide phosphor, for example, is a point on the lattice of a zinc sulfide crystal where a molecule or a minute crystal of copper sulfide is adsorbed.² Since the lattices are different, there is a

¹ See p. 124.

² SCHLEEDE and GANTZCKOW [Z. physik. Chem., 106, 37 (1923)] assume that a copper ion replaces a zinc ion in the lattice.

condition of strain at the interface which makes it easier for light to displace certain electrons. This condition of strain is augmented by distorting the lattice of the zinc sulfide by rapid cooling of the ignited substance.¹ This concept of a center of phosphorescence accounts for a number of facts without the necessity of resorting to improbable assumptions:

Let us consider, first of all, the quantity of heavy metal impurity involved in the luminescence process, taking the zinc-copper phosphor as an example. In this case, 0.000006 gram of copper per gram of zinc sulfide, or approximately 9 molecules of copper sulfide for every one million of zinc sulfide, is sufficient to produce a distinct phosphorescence. It has been demonstrated repeatedly that a good phosphor is made up of fairly large crystals, the result of ignition for 30 minutes to 1 hour at temperatures above 1000°. Indeed, Schleede² was unable to obtain a good phosphor with crystals sufficiently small to give an x-radio-gram with unbroken interference bands, using the Debye method. If the crystals in a good zinc phosphor vary in size from 0.01 to 0.1 millimeter in length, as observations disclose,³ it is obvious that the light which strikes but a portion of the surface of the crystals will affect but a small portion of the total mass of the phosphor. When one considers that the luminescence bands are due entirely to the copper sulfide and that 9 copper sulfide molecules per million of zinc sulfide is sufficient, it seems altogether improbable that the few molecules of copper sulfide on the surface would account for the quantity of light emitted, assuming that the copper sulfide is dissolved, that is, distributed uniformly throughout the mass. On the other hand, if minute crystals of copper sulfide are adsorbed at points on the surface, which are not large for a given mass because of the size of the crystals, it is more easy to understand how such a small amount of active impurity can be so effective.

This view of the nature of a center of phosphorescence also accounts for the fact that a comparatively small amount of

¹ TOMASCHEK: *Ann. Physik*, [4] **65**, 193 (1921); SCHLEEDE and GANTZCKOW: *Z. physik. Chem.*, **106**, 37 (1923).

² SCHLEEDE and GANTZCKOW: *Z. physik. Chem.*, **106**, 44 (1923).

³ TOMASCHEK [*Ann. Physik*, [4] **65**, 194 (1921)] gives 0.003 to 0.10 millimeter but the lower limit was doubtless attained by short ignition at a comparatively low temperature which does not yield the best phosphors.

copper sulfide will destroy the phosphorescence completely. A uniformly distributed layer of black copper sulfide on the surface will not only cause an even distribution of strain over the surface but will prevent the light from reaching the sensitive interface. Moreover, this view accounts for the observed variation in the maximum amount of copper sulfide which will yield a good phosphor. Other things remaining constant, the maximum amount will be higher the smaller the crystals, that is, the greater the surface for a given mass. Finally, this concept accounts for the fact that grinding a phosphor cuts down or destroys the phosphorescence: the active surfaces are covered over with inactive powder during the grinding process.

The Phosphorescence Process.—In general, the pure substances of which a sulfide phosphor is composed are stable in the presence of ultraviolet light. Considering once more the zinc-copper phosphor, it has been found that zinc sulfide is decomposed by light only in the presence of zinc ions¹ and copper sulfide is quite stable. But when light strikes a zinc sulfide-copper sulfide interface where there is a condition of strain, electrons are split off from sulfur ions and taken up by copper ions, giving elementary copper and sulfur which recombine with the emission of light, during excitation (flourescence) and after the exciting light is removed (phosphorescence). If one objects to the assumption that the rearrangement of electrons by the action of ultraviolet light always results in the liberation of the elementary substances, the alternative is to assume that the electrons are displaced in the direction which would lead to the liberation of the elements if the energy applied were sufficiently great. In any event, the exciting light induces a chemical change which is essentially a reduction process, the subsequent oxidation causing the luminescence.

APPLICATIONS

The most important technical use of the phosphorescent sulfides is in the manufacture of luminous paints. For this purpose, a phosphorescent calcium sulfide was first used by Balmain about 1877 on watch and clock dials, etc. Since it was necessary to expose the articles to light in order to render the

¹ Cf. WEISER and GARRISON: *J. Phys. Chem.*, **31**, 1237 (1927).

paint effective, Balmain's paint has been largely replaced by self-luminous paints which consist of phosphors, usually of zinc sulfide¹ mixed with a small amount of radioactive substance, the α -rays from which excite luminescence.² Probably the best radioactive substance to use is radium itself³ although the cheaper mesothorium or radiothorium may be employed.⁴ Commercial products contain from 30 to 300 micrograms of radium per gram of zinc sulfide. The luminescence of the phosphors are roughly proportional to the radium content, but the rate of decay of the phosphorescence is likewise proportional to the radium content, so that phosphors containing the most radium are brightest at the outset but show the most rapid falling off in intensity of glow. The decay in luminescence is due to the destruction of the phosphorescent centers by continuous bombardment of the α particles. The relation between the brightness of luminescence and the time is a hyperbolic one.⁵

To use the luminous material, it is mixed with a suitable vehicle usually some form of clear transparent varnish, the resulting thick paint being applied by means of a fine stiff hand brush or a stylus. Paper, porcelain, mica, and metal discs of all sorts bearing figures, lines, or diagrams are now treated with the paint. For some instruments, such as those used on airplanes and gun sights, the requirement of luminosity outweighs other considerations of cost and effective life; hence, preparations are employed which have a relatively high radium content. For many purposes, however, such as the use on marching compasses, wrist watches, push buttons, etc., preparations possessing a lower initial luminosity are quite satisfactory and such material has the advantage of lower cost and longer life. Francis⁶ has outlined a procedure for recovering radium from a luminous paint after it no longer functions.

¹ Cf., however, PRAGER: *Chem. Abstr.*, **15**, 2003 (1921).

² BECQUEREL: *Compt. rend.*, **129**, 912 (1899); **137**, 629 (1903); CURIE and DEBIERNE: *Ibid.*, **133**, 931 (1901); CURIE: *J. chim. phys.*, [7] **1**, 409 (1903); *Physik. Z.*, **5**, 281, 313, 345 (1904).

³ VIOL and KAMMER: *Trans. Am. Electrochem. Soc.*, **32**, 381 (1917).

⁴ BERNDT: *Chem. Ztg.*, **45**, 505 (1921); BAHR: *Chem. Abstr.*, **10**, 2840 (1916).

⁵ DORSEY: *Trans. Am. Electrochem. Soc.*, **32**, 389 (1917).

⁶ *J. Soc. Chem. Ind.*, **41**, 94 T (1922).

Phosphorescent sulfides may be used to coat the back of artificial pearls, paste diamonds, rubies, emeralds, opals, etc., causing them to exhibit a change in color in twilight and to be luminous in the dark.¹ The use of phosphors for lighting may be accomplished by coating a vacuum tube containing rarefied nitrogen, argon, or air which is excited by a high-frequency current.² The efficiency of the process is not reported but it is probably quite low.

Scientifically, phosphorescent zinc sulfide is employed in the spinthariscope and in phosphorescent light screens³ which are used in investigating the properties of x-rays⁴ and canal rays.⁵ Miethe⁶ obtained direct photographic positives by means of luminescent zinc sulfides.

¹ SAUVAGE: British Patent, 176687 (1921).

² RISLER: British Patents, 207786, 208723 (1923).

³ CROOKES: *Chem. News*, **87**, 241 (1903); RUTHERFORD and GEIGER: *Proc. Roy. Soc. (London)*, **81A**, 141 (1908); GIESEL: *Ber.*, **35**, 3610 (1910).

⁴ DANNEBERG: *Physik. Z.*, **8**, 787 (1907).

⁵ BAERWALD: *Ann. Physik*, [4] **39**, 866 (1912).

⁶ German Patent, 352165 (1922).

II
COLLOIDAL SULFATES

CHAPTER XI

THE COLLOIDAL SULFATES OF BARIUM, STRONTIUM, AND LEAD

COLLOIDAL BARIUM SULFATE

THE PRECIPITATED SALT

The effect of the concentration of the interacting solutions on the physical character of precipitated barium sulfate has been studied in detail by von Weimarn and an account of his observations is recorded in Chap. I. The solubility of the salt is appreciable, 0.0024 gram per liter at 18°; hence, on mixing the ordinary laboratory solutions of barium salts and sulfates, barium sulfate is obtained as a more or less immediate crystalline precipitate. On the other hand, if the concentrations of the interacting solutions are quite high, there results an enormous number of extremely minute particles which adsorb water yielding a gelatinous precipitate or a jelly. The gels formed in this way change spontaneously into granular precipitates on standing for a short time. Kato¹ obtained much more stable gels by the interaction of sulfuric acid and barium acetate in an alcohol-water mixture in which barium sulfate is much less soluble than in water alone. Similarly, Lenher and Taylor² prepared stable gels by the interaction of dilute solutions of barium chloride and sulfuric acid in selenium oxychloride, in which barium sulfate is almost entirely insoluble. Careful observations disclose that selenium oxychloride is without action on polished surfaces of barite. Moreover, it has been shown that selenium oxychloride does not penetrate barium sulfate crystals. The evidence appears conclusive, therefore, that gelatinous barium sulfate obtained by means of selenium oxychloride is merely barium sulfate made plastic by adsorbed selenium oxychloride. This

¹ *Mem. Coll. Sci. Kyoto Imp. Univ.*, **2**, 187 (1909-10).

² *J. Phys. Chem.*, **28**, 962 (1924).

accords with the author's view¹ that a gelatinous precipitate consists of very finely divided solid particles which have adsorbed the liquid strongly. The greater stability of the alcogels and selenium oxychloride gels as compared with the aqueous gels is due both to the lower solubility of barium sulfate in the organic liquids and to the fact that the salt adsorbs the organic liquids more strongly than water. This is not true of all organic liquids. Thus, when barium sulfate is shaken with a mixture of water and heptane the salt concentrates in the dimeric interface, indicating that the adsorption of the two liquids is of the same order. On the other hand, when the salt is shaken with a mixture of heptane and selenium oxychloride it concentrates in the selenium oxychloride layer and when shaken with a mixture of selenium oxychloride and 70 per cent sulfuric acid it collects in the acid layer.

While the degree of supersaturation as determined by the concentration of the reacting ions and the solubility of the resulting salts is of primary importance in determining the physical character of precipitates, it is well known to analytical chemists that the physical condition of precipitates is influenced to a marked degree by the presence of other substances in solution. Thus, barium sulfate comes down in a more finely divided state when precipitated with sulfate in excess than when precipitated with barium in excess.² Since, in general, any substance which is adsorbed by a second will tend to peptize the latter, it follows that, other conditions being the same, barium sulfate will come down most finely divided when precipitated in the presence of those substances which it adsorbs most strongly.³ Now barium sulfate adsorbs its own ions strongly and hydrogen ion is adsorbed more strongly than most cations. Accordingly, when sulfuric acid is treated with barium chloride in excess, the precipitate tends to come down in a finely divided state because of the relatively strong adsorption of barium and hydrogen ions. This effect is sufficiently great to peptize the salt as a positive sol under suitable conditions. The precipitate would come down in a very finely divided form with sulfuric acid in excess were it

¹ WEISER: "The Hydrous Oxides," 23 (1926).

² FOULK: *J. Am. Chem. Soc.*, **18**, 803 (1896).

³ WEISER: *J. Phys. Chem.*, **21**, 314 (1917).

not for the fact that the strongly adsorbed hydrogen ion neutralizes the adsorption of sulfate. With potassium sulfate in excess, the precipitate is finer than with sulfuric acid in excess since potassium ion is not strongly adsorbed. The presence of hydrochloric acid tends to give a coarser precipitate because of the solvent action of the acid.

Since the analyst is usually called upon to determine sulfate rather than barium, the question of getting the barium sulfate in the proper physical condition for quantitative filtration has received considerable attention. A readily filterable precipitate is ordinarily obtained by adding the barium salt drop by drop with vigorous stirring to the boiling sulfate solution containing a small amount of hydrochloric acid. Since the solubility of barium sulfate is increased greatly by the presence of hydrochloric acid, the concentration of the latter is ordinarily kept quite low. Murmann¹ points out that complete precipitation results in the presence of a relatively large amount of hydrochloric acid provided ethyl alcohol is added and the filtration carried out in the cold.

While slow addition of barium chloride to the hot sulfate solution acidified slightly with hydrochloric acid ordinarily yields a granular, readily filterable salt, an occasional precipitate is obtained which is too fine to be retained, even by a close filter. It is common practice to digest such a precipitate at the boiling point until it takes on the desired physical character. The coalescence of barium sulfate precipitates by digestion is ordinarily attributed to the growth of larger particles at the expense of smaller, but Trimble² showed that the solution pressure of barium sulfate at about 100° ceases to be a function of particle size for particles larger than about 2μ in diameter. Odén³ boiled a suspension of barium sulfate for 100 hours and observed that the number of particles under 0.2μ in radius was decreased only from 47 to 30 per cent. The observed coalescence by digestion in the mother liquor is apparently due to the collection of the particles into relatively larger clumps, followed by the cement-

¹ *Oesterr. Chem. Ztg.*, **13**, 227 (1911); *Chem. Abstr.*, **5**, 2382 (1911).

² *J. Phys. Chem.*, **31**, 601 (1927).

³ *Svensk Kem. Tid.*, **32**, 74, 90, 108 (1920); *Chem. Abstr.*, **15**, 971 (1921).

ing together of the unit particles into aggregates which are retained by the filter. To speed up the growth of larger particles at the expense of smaller ones, Krak¹ recommends pouring off the supernatant liquid and adding 10 cubic centimeters of saturated ammonium acetate solution, the solvent action of which causes the particles to grow to readily filterable dimensions.² Kaus³ claims that the addition of macerated filter paper, to which the minute particles cling, is effective in preventing the precipitate from running through.

It has been observed by Hulett⁴ and confirmed by Dundon⁵ that finely ground barium sulfate added to a saturated solution of the salt caused an increase in conductivity which rose to a maximum and then decreased slowly, finally approaching that of the normally saturated solution. This changing conductivity is usually attributed to changing solubility with size of particles; but Balarew⁶ questions whether the greater solubility of smaller particles is the important factor. He attributes the increase in electrical conductivity on rubbing crystals of barium sulfate in contact with the saturated solution to (1) the presence of barium chloride in the sulfate, (2) the greater solubility of broken than of complete crystals, and (3) the breaking up of atomic aggregates. The subsequent fall in conductivity could be due partly to the crystallizing out of barium sulfate on account of the solution of the chloride; but the velocity of crystallization is much greater than the rate of fall of conductivity so that the latter is attributed to the slow restoration of equilibrium between the complete and broken crystals. While the greater solubility of broken crystals may be the determining factor in the experiment referred to, there is no doubt but that below a certain size, the solution pressure of smaller particles is greater than that of larger ones. Balarew raises but does not settle the question as to whether Hulett's experimental method gives a true measure of the change in solubility with crystal size.

¹ *Chemist-Analyst*, **5**, 26 (1912).

² OSBORNE: *J. Phys. Chem.*, **17**, 629 (1913).

³ *Chemist-Analyst*, **6**, 9 (1913).

⁴ *Z. physik. Chem.*, **37**, 385 (1901).

⁵ *J. Am. Chem. Soc.*, **45**, 2658 (1923).

⁶ *Z. anorg. Chem.*, **145**, 122 (1925); **163**, 213 (1927).

The degree of subdivision of precipitated barium sulfate employed as a pigment is measured either by determining the rate of setting or by determining the height of the sediment after a given time.¹ The effect of salts on the sedimentation is marked. Thus, a quantity of barytes which settled in water to a height of 47 millimeters in 2 days, occupied a height of only 37 millimeters when allowed to settle in 10 per cent sodium chloride under the same conditions. This effect was reversed by washing out the salt solution. Similarly, barytes which settled to a height of 23 millimeters in 1 day in the presence of barium chloride, still occupied 51 millimeters after 5 days in the absence of barium chloride. Usually barium sulfate settles sharply without an opalescent region above the sediment, but in the presence of barium chloride, opalescence is produced, indicating peptization of the barium sulfate. An opalescent supernatant liquid is also produced in the presence of protecting agents, such as glycerin and gelatin.

ADSORPTION BY BARIUM SULFATE

Because of the intrinsic importance of barium sulfate in quantitative analysis, its adsorptive power has been the subject of numerous investigations. A quantitative study of the contamination with barium chloride² of the salt formed by precipitation of barium chloride by sulfuric acid and of sulfuric acid by barium chloride has been made by Richards and Parker³ and by Hulett and Duschak.⁴ The latter investigators find that barium chloride is taken up not only during precipitation but also when finely divided crystals are suspended in a solution of barium chloride. As an explanation of the phenomenon, they consider the possible formation of complex salts such as BaClHSO_4 and $(\text{BaCl}_2)_2\text{SO}_4$.⁵ Schneider⁶ investigated quantitatively the contamination of barium sulfate by ferrous sulfate and Creighton⁷

¹ LIESEGANG: *Farben-Ztg.*, **29**, 334 (1923).

² Cf. TESCHEMACHER and SMITH: *Chem. News*, **24**, 61, 66 (1871).

³ Z. *anorg. Chem.*, **8**, 413 (1895).

⁴ Z. *anorg. Chem.*, **40**, 196 (1904).

⁵ Cf. FOLIN: *J. Biol. Chem.*, **1**, 131 (1906).

⁶ Z. *physik. Chem.*, **10**, 425 (1892); cf. GLENDINNING and EDGER: *Chem. News*, **24**, 140 (1871); SLOANE: *Ibid.*, **44**, 221 (1882); JANNASCH and RICHARDS: *J. prakt. Chem.*, [2] **39**, 321 (1889).

⁷ Z. *anorg. Chem.*, **63**, 53 (1909).

made a similar study of the contamination with aluminum sulfate. Both Schneider and Creighton regard the phenomenon as a case of solid solution, while Richards¹ compared the contamination with ferric sulfate to the occlusion of hydrogen by palladium, a phenomenon which probably involves both solid solution and adsorption. The work of Küster and Thiel² and of Korte,³ who repeated and extended Schneider's experiments, indicates, however, that the contamination is an adsorption phenomenon. Indeed, the adsorption theory seems to offer the only plausible explanation of the fact that barium sulfate carries down all manner of substances from either true⁴ or colloidal solutions,⁵ and most investigators subscribe to this explanation of the contamination.⁶ Thus, from precise observations on the carrying down of a large number of cations by barium sulfate, Johnston and Adams⁷ conclude:

Since the size of the crystal particles depends on the degree of supersaturation, it follows that the degree of fineness of the particles is increased by a rapid addition of the precipitant, is diminished by precipitating in a medium in which barium sulfate is more soluble, and is further diminished when the precipitate remains in contact with a medium in which it is soluble by the process of crystallization, the ratio of which depends on this solubility. Now these are precisely the conditions which affect the occlusion when precipitations are made from identical solutions. We are therefore justified in concluding that this occlusion is a phenomenon of adsorption at the surface of the grains of the precipitate and that its amount depends upon (*a*) the composition of the original solution and (*b*) the initial fineness of the precipitate and the amount of recrystallization which has taken place.

¹ *Z. anorg. Chem.*, **23**, 383 (1900).

² *Z. anorg. Chem.*, **19**, 97 (1899); **22**, 424 (1900).

³ *J. Chem. Soc.*, **87**, 1503 (1905).

⁴ PATTEN: *J. Am. Chem. Soc.*, **25**, 186 (1903).

⁵ VANINO and HARTL: *Ber.*, **37**, 3620 (1904).

⁶ WOHLERS: *Z. anorg. Chem.*, **59**, 203 (1908); ALLEN and JOHNSTON: *J. Am. Chem. Soc.*, **32**, 588 (1910); JOHNSTON and ADAMS: *Ibid.*, **33**, 829 (1911); WEISER: *J. Phys. Chem.*, **21**, 317 (1917); KOELSCH: *Chem. Ztg.*, **43**, 117 (1919); ODÉN: *Arkiv. Kemi, Mineral. Geol.*, **7**, No. 26, p. 92 (1920); DHAR, SEN, and CHATTERJI: *Kolloid-Z.*, **33**, 29 (1923); cf., however, SMITH: *J. Am. Chem. Soc.*, **39**, 1152 (1917); KOLTHOFF and VOGELZANG: *Z. anal. Chem.*, **58**, 49 (1919).

⁷ *J. Am. Chem. Soc.*, **33**, 829 (1911).

Adsorption of Cations.—The first systematic study of the adsorption by barium sulfate of a large number of cations under strictly comparable conditions was made by Johnston and Adams. The results of their observations as recorded in Table XXIX give the amounts in millimols and milliequivalents of the sulfates of the various metals adsorbed by 1 gram of barium sulfate when precipitated from solutions about 0.003 normal in hydrochloric acid and containing the metallic chlorides in the initial concentration $A = 0$ and $B = 0.1$ normal. The time of precipitation was

TABLE XXIX.—ADSORPTION OF CATIONS BY BARIUM SULFATE

Metal	Sulfate adsorbed by 1 gram of BaSO ₄			
	A		B	
	Milli-equivalents	Millimols	Milli-equivalents	Millimols
Magnesium.....	0.048	0.024		
Lithium.....	0.033	0.033	0.040	0.040
Sodium.....	0.029	0.029	0.043	0.043
Potassium.....	0.033	0.033	0.035	0.035
Aluminum.....	0.051	0.017	0.060	0.020
Iron (ferrous).....	0.074	0.037	0.120	0.060
Nickel.....	0.062	0.031	0.100	0.050
Copper.....	0.082	0.041	0.100	0.050
Zinc.....	0.080	0.040	0.100	0.050
Manganese.....	0.128	0.064	0.160	0.080
Cadmium.....	0.160	0.080	0.180	0.090

4 minutes and the time of standing 4 hours. The adsorption values obtained under these conditions are of the same order of magnitude; nevertheless, they show considerable variation. If the values are expressed in equivalents, one can detect the tendency for ions of higher valence to be more strongly adsorbed in accord with Schulze's law. This tendency is less marked when the adsorption values are expressed in mols. Moreover, when so expressed, the adsorption of trivalent aluminum is less than that of either the univalent or divalent ions. In this respect aluminum appears quite different from trivalent lanthanum which

Frion¹ found to be adsorbed much more strongly than divalent magnesium.

Germann² studied the adsorption of radium by barium sulfate and showed that the same laws of adsorption which apply to the adsorption of ponderable masses are applicable with an equal degree of accuracy to masses as small as 5×10^{-8} grams adsorbed per gram of adsorbent. The observations were made by adding a known amount of radium-free barium sulfate to 80 cubic centimeters of a standard solution of radium barium chloride, which was allowed to stand until adsorption equilibrium was established, after which the barium sulfate was filtered off and the supernatant liquid analyzed for the radium content by the emanation method. The data are reproduced in Table XXX. These data are in accord with Freundlich's adsorption formula $\frac{X}{M} = Kc^n$ where X is the amount adsorbed by mass M of adsorbent, c the equilibrium concentration and K and n constants, as evidenced by the fact that a straight line is obtained by plotting $\ln \frac{X}{M}$ against $\ln c$ (Fig. 17).

TABLE XXX.—ADSORPTION OF RADIUM BY BARIUM SULFATE

BaSO ₄ employed, grams	Equilibrium concentration of Ra after adsorption, grams per cubic centimeter $\times 10^{10}$	Decrease in radium con- centration due to adsorp- tion, grams per cubic centi- meter $\times 10^{10}$
0.0	22.79	0.00
0.05	18.55	4.24
0.10	15.12	7.67
0.20	9.47	13.32
0.30	5.86	16.93
0.40	3.97	18.82
0.50	2.70	20.09

In addition to radium, the active substance adsorbed by barium sulfate when it is precipitated in solutions containing the radioactive constituents of uranium ores, is chiefly ionium³,

¹ *J. chim. phys.*, **7**, 101 (1909).

² *J. Am. Chem. Soc.*, **43**, 1615 (1921).

³ KAMMER and SILVERMAN: *J. Am. Chem. Soc.*, **47**, 2514 (1925).

accompanied by a relatively small amount of actinium and not actinium alone as claimed by Debierne.¹ Strong adsorption of ionium by barium sulfate is indicated by the fact that the salt has an extraordinary strong capacity to adsorb thorium, the isotope of ionium.

Paneth² and Horovitz³ observed that radium is strongly adsorbed by barium sulfate and barium chromate, whereas it is not adsorbed at all by hydrous chromic oxide and silver chloride.

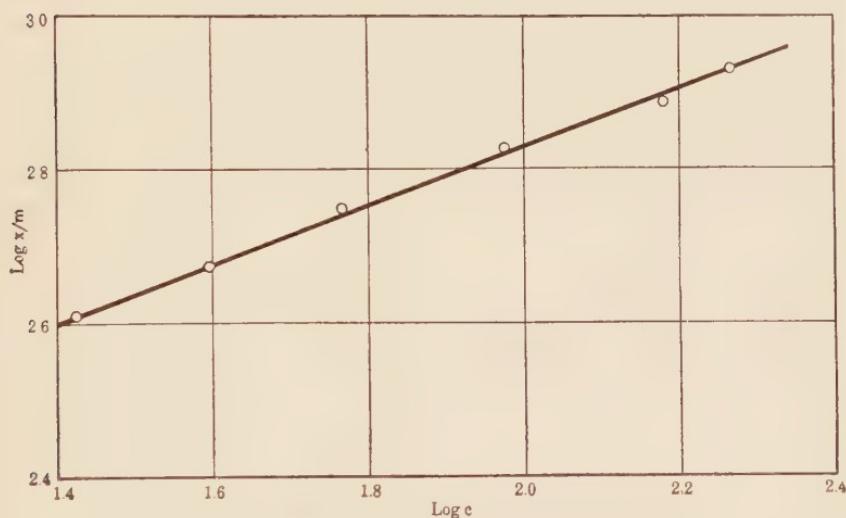


FIG. 17.—Adsorption of radium by barium sulfate.

Since radium sulfate and radium chromate are soluble, whereas radium oxide and radium chloride are not, Paneth was led to conclude that those ions will be relatively strongly adsorbed whose compounds with the oppositely charged ions of the ion lattice are slightly soluble. As we shall see, this conclusion known as Paneth's adsorption rule is, at best, little more than a first approximation.⁴ Thus, thorium is adsorbed more strongly than radium by barium sulfate although thorium sulfate is fairly soluble.

¹ *Compt. rend.*, **129**, 593 (1899); **130**, 906 (1900).

² *Physik. Z.*, **15**, 924 (1914).

³ HOROVITZ and PANETH: *Z. physik. Chem.*, **89**, 513 (1915).

⁴ See p. 187 and especially p. 217.

Adsorption of Anions.—When an alkali sulfate is precipitated with barium chloride in excess, the most usual analytical procedure, the determinations are too low, since some sulfate is weighed as alkali sulfate and calculated as if it were pure barium sulfate. Opposed to this is the adsorption of chloride, probably as barium chloride, which tends to make the analytical results too high. The latter effect manifests itself especially in the precipitation of sulfuric acid by barium chloride and of barium chloride by sulfuric acid. Hulett and Dusehak¹ found it possible to obtain exact results in such determinations by estimating the chlorine content of the precipitate and deducting the barium chloride equivalent from the weight of the crude barium sulfate.

Although the adsorption of chloride ion by barium sulfate is appreciable, Mendelejeff² long ago showed it to be small compared to that of nitrate. This was confirmed in the author's laboratory³ in the course of an investigation of adsorption of various ions by barium sulfate formed on mixing sodium sulfate with a definite excess of the barium salts of the respective ions. The extent of the adsorption was determined by direct analysis of the washed precipitate. In Table XXXI the ions are arranged in the order of equivalent adsorption, beginning with the most strongly adsorbed ferrocyanide. The adsorption in mols and the solubility of the several barium salts is also included in the table. From a consideration of the absolute amount of the adsorption in each case, there is little to suggest Schulze's law. For although a quadrivalent ion appears to be adsorbed most strongly, there are four univalent ions more strongly adsorbed than trivalent ferricyanide. Furthermore, contrary to what is implied in Schulze's law, there is a wide variation in the amount of univalent ions adsorbed, nitrate being carried down 150 times more strongly than iodide.

Considering the relationship between the solubility of the several barium salts and the adsorbability of the respective anions by barium sulfate, one can note a tendency for the anions of the less soluble salts to be more strongly adsorbed, in accord

¹ Z. anorg. Chem., **40**, 196 (1904); cf. KARAOGLANOW: Z. anal. Chem., **57**, 77 (1918).

² Pogg. Ann., **55**, 214 (1842).

³ WEISER and SHERRICK: J. Phys. Chem., **23**, 205 (1919); cf. GHOSH and DHAR: Kolloid-Z., **35**, 144 (1924).

TABLE XXXI.—ADSORPTION OF ANIONS BY BARIUM SULFATE

Anion	Adsorption by 100 mols BaSO ₄		Solubility of barium salts, millimols per gram water at 25°
	Gram equivalents	Gram mols	
Ferrocyanide.....	13.20	3.30	0.07
Nitrate.....	8.48	8.48	0.40
Nitrite.....	7.47	7.47	3.10
Chlorate.....	5.84	5.84	1.25
Permanganate.....	2.85	2.85	1.93
Ferricyanide.....	2.70	0.90	very soluble
Chloride.....	1.76	1.76	1.78
Bromide.....	0.83	0.83	3.57
Cyanide.....	0.31	0.31	4.25
Sulfocyanate.....	0.22	0.22	6.13
Iodide.....	0.06	0.06	5.43

with Paneth's rule. There are, however, a number of exceptions, even to this qualitative statement. Thus nitrate and nitrite ions are adsorbed to approximately the same extent although the former is but one-eighth as soluble as the latter.

Although chemically dissimilar ions of the same valence may show a wide variation in the degree of adsorption, thus indicating that adsorbability is a specific property of ions, the similarity in the adsorption of nitrate and nitrite ions which are more nearly related chemically suggests that the adsorption of ions by a given disperse phase is determined by two factors, the specific adsorbability of the ion, in which the solubility of the salt formed with the opposite ion of the crystal lattice may be an important factor, and the valence of the ion. By choosing a series of ions of much the same general character, thus minimizing the specific factor, it is possible to emphasize the effect of valence. For example, a comparison of the adsorption of various cyanides by barium sulfate discloses an unmistakable tendency for ions of higher valence to be adsorbed most strongly, irrespective of whether the adsorption is expressed in equivalents or mols.

It should be pointed out that the data on adsorption of various ions by barium sulfate will be strictly comparable only in case

TABLE XXXII.—EFFECT OF VALENCE ON THE ADSORPTION OF ANIONS BY BARIUM SULFATE

Anion	Valence	Adsorption value, gram equivalents per 100 mols BaSO ₄
Ferrocyanide.....	4	13.20
Ferricyanide.....	3	2.70
Sulfocyanate.....	1	0.22
Cyanide.....	1	0.31

the size of the particles of the adsorbent is the same in all experiments. It is probable that this is approximately true in the above experiments since the conditions of precipitation were maintained constant. Estrup¹ determined the adsorption of permanganate by barium sulfate of varying degrees of dispersion, obtained by precipitating the salt with equivalent solutions of barium chloride and potassium sulfate which varied in concentration between *N*/100 and *N*/1000. It was found that, irrespective of whether the permanganate was added before or after the precipitation of the barium sulfate, the amount adsorbed reached a minimum and then increased again with increase in the dilution of the solution from which the barium sulfate separated. Since the size of particles increases continuously with decreasing concentration of the interacting solutions, it is not at all clear what Estrup's data mean. It is possible that his experimental method was inaccurate and the observations should be repeated.

The precipitation of barium sulfate in the presence of potassium permanganate is said by Grimm² to give well-defined mixed crystals of a red color which are not decolorized by being warmed with oxalate for 2 months. Balarew and Janakiewa³ obtained a similarly colored product by allowing potassium sulfate in saturated potassium permanganate to diffuse through a porous cup into barium chloride solution saturated with potassium permanganate; but this product was completely decolorized by washing with oxalate and at the same time broke up into minute prisms.

¹ *Kolloid-Z.*, **7**, 299 (1910).

² *Z. Elektrochem.*, **30**, 467 (1924).

³ *Z. anorg. Chem.*, **156**, 301 (1926).

Since mixed crystal formation should not be prevented by a change in the velocity of crystallization, the obvious conclusion is that the red precipitate is not homogeneous but consists of minute prisms of barium sulfate colored by adsorbed permanganate.

On account of the adsorption of both positive and negative ions by barium sulfate and the effect of acids and salts on its solubility, the precise determination of sulfate as the barium salt is best accomplished by choosing the conditions so that errors due to adsorption and to solubility compensate each other.¹ A large percentage of the adsorbed impurity may be eliminated by treating the crude precipitate with a small amount of sulfuric acid in which the salt dissolves as $H_2Ba(SO_4)_2$ ² and then reprecipitating by pouring the sulfuric acid solution into cold water. Unfortunately, the precipitate obtained in this way is frequently so finely divided that quantitative filtration can be accomplished only after prolonged digestion.

BARIUM SULFATE SOLS

Von Weimarn obtained momentary sols of barium sulfate by mixing solutions of barium thiocyanate and manganese sulfate of approximately 0.0008 normality. In spite of the dilution, the particles agglomerate and settle out in a short time. Kato³ diluted a 1 molar solution of sulfuric acid with twice its volume of alcohol and added it to an equivalent amount of a molar solution of barium acetate diluted with five times its volume of alcohol. On evaporating the resulting gelatinous precipitate and milky sol to dryness under reduced pressure below 40°, a translucent casein-like residue was obtained which was readily and completely dispersed in water to a stable fluorescent sol. The sol is positively charged and shows the usual precipitation reaction towards anions. Cations of high valency stabilize the sol, barium chloride and nitrate precipitating it only in highly concentrated-solutions.—Recoura⁴-prepared - a similar sol by mixing equivalent solutions of barium ethylate and sulfuric acid dissolved in pure glycerin and then diluting with water.

¹ Cf. JOHNSTON and ADAMS: *J. Am. Chem. Soc.*, **33**, 829 (1911).

² MEYER and FRIEDRICH: *Z. physik. Chem.*, **101**, 498 (1922).

³ *Mem. Coll. Sci., Kyoto Imp. Univ.*, **2**, 187 (1909-10).

⁴ *Compt. rend.*, **146**, 1274 (1908).

The fact that the interacting substances were mixed in stoichiometric proportions does not change matters, since it is known that barium ion is so strongly adsorbed that it is always present in barium sulfate precipitates, even when the latter are precipitated in the presence of a slight excess of soluble sulfate. This is further shown by some observations of Gyemant¹ on the effect of the concentration of barium ion on the electrokinetic potential, ξ , at the interface barium-sulfate water. The ξ -potential was determined from electroendosmotic data by substituting in the formula:²

$$\xi = \frac{4\pi\eta M}{DI\sigma}$$

where η is the viscosity at room temperature, M the volume of liquid transferred through the diaphragm in unit time, D the dielectric constant, I the current strength, and σ the specific resistance of the liquid. The data are recorded in Table XXXIII and represented graphically in Fig. 18. The concentration of barium ion and also of sulfate ion is expressed by the notation commonly used for designating hydrogen ion values. pBa is

TABLE XXXIII

pBa	M , cubic centi- meters per minute	σ , ohms	I, milliamperes	ξ millivolts
0.3	12.0	12.9	60.0	+36.4
1.0	62.0	63.0	46.0	+50.3
2.0	145.0	437.6	14.0	+55.6
3.0	92.0	3,196.0	4.0	+22.0
3.5	33.0	9,416.0	1.7	+ 4.8
4.0	31.0	23,440.0	1.7	+ 1.8
5.0	22.0	24,000.0	1.7	+ 1.3
6.0	13.0	16,782.0	1.7	+ 1.0
7.0	0.0	0.0
8.0	20.5	486.0	12.0	- 8.6
9.0	12.7	78.5	43.2	- 8.8
9.7	4.5	18.0	63.0	- 9.3

¹ Z. physik. Chem., 103, 260 (1922).² Cf. p. 27.

therefore the negative logarithm of the concentration of barium ion. Since the solubility product of barium sulfate is 10^{-10} , $p\text{Ba} + p\text{SO}_4 = 10$. The concentration of barium ion in the solution was varied by adding barium chloride or sodium sulfate. At $p\text{Ba} = 7$, that is $\frac{M}{1000} \text{Na}_2\text{SO}_4$, the cataphoretic migration velocity is zero. This therefore represents the point

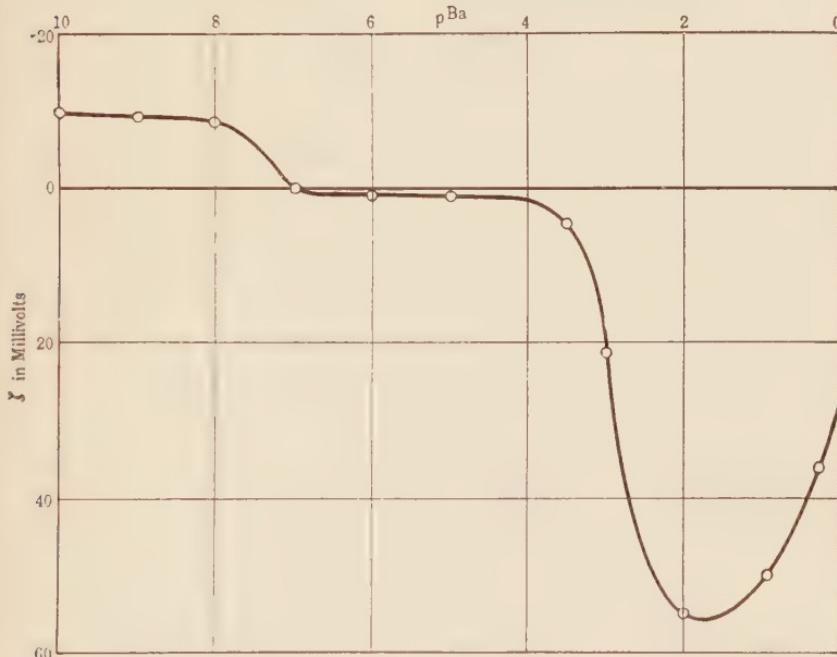


FIG. 18.—Influence of the concentration of barium ion on the electrokinetic potential at the interface barium sulfate-water.

of reversal of the ζ -potential. The curve runs nearly parallel to the abscissa axis to $p\text{Ba} = 4$, then falls sharply to a minimum which lies at approximately $p\text{Ba} = 2$. It is obvious, of course, that the curve does not represent the dependence of the ζ -potential on the barium ion concentration only, since it is impossible to vary the barium ion concentration without, at the same time, changing the anion concentration and, in the case at hand, the nature of the anion also. Thus, to the left of $p\text{Ba} = 5$, the sulfate ion concentration increases and to the right the chloride ion con-

centration increases. The adsorption of the anions unquestionably modifies the course of the $p\text{Ba}-\xi$ curve.

Since the charge on the barium sulfate particles becomes negative when the sulfate ion concentration of the surrounding liquid is above $\frac{M}{1000}$ it should be possible to prepare a stable negative sol in the presence of sulfate or other readily adsorbed anion. Such a sol is obtained by adding a slight excess of $N/10$ potassium sulfate to $N/10$ barium chloride using as solvent 1 part of water to 5 parts of glycerin.¹ A negative hydrosol is also obtained by double decomposition of barium salts and sulfates in the presence of sodium citrate. Such sols are almost clear and Spiller² believed them to be true solutions of a double salt of barium sulfate and citrate. Nichols and Thies³ showed, however, that the apparent solutions are merely negatively charged dispersions of barium sulfate in which the particles are in an extremely fine state of subdivision. Quantitative estimations involving the precipitation of barium sulfate can be made in the presence of citrates, provided slightly more than enough acid is added to convert the citrates into citric acid, thereby cutting down the concentration of citrate ion below the point necessary for peptization of barium sulfate.

Feilmann⁴ prepared a sol of barium sulfate by precipitation in a slightly alkaline solution of commercial casein. Since the reaction of the sol towards acid and alkalies is that of casein, it is obvious that the colloidal barium sulfate is surrounded by a protecting film of proteid.

The sols of barium sulfate are faintly opalescent to distinctly milky in appearance, depending on the concentration and the size of particles. Beechhold and Hebler⁵ investigated nephelometrically the connection between turbidity and the size of suspended particles of barium sulfate in various mixtures of ethyl alcohol and glycerin. Observations disclose that, for suspensions containing the same amount of barium sulfate but of varying degrees of dispersion, the turbidity increases from 2.5μ .

¹ WEISER: *J. Phys. Chem.*, **21**, 318 (1917).

² *J. Chem. Soc.*, **10**, 110 (1858).

³ *J. Am. Chem. Soc.*, **48**, 303 (1926).

⁴ *Chem. News*, **98**, 310 (1908).

⁵ *Kolloid-Z.*, **31**, 70 (1922).

downwards. The maximum turbidity is reached with particles of about $800\mu\mu$ for white light, that is, in the region of the extreme red. Further reduction of particle size caused a marked decrease in turbidity. Rayleigh's law $I = K \frac{nv^a}{\lambda^4}$, in which I is the intensity of the scattered light, n the number of particles per unit volume, v the volume of the particles, λ the wave length of the light, and K a constant, holds only for the region of size below $800\mu\mu$. If a standard sol of known turbidity is available, it is possible to estimate the size of amicrons and submicrons from the relation between turbidity and particle size.

Owe¹ showed that the turbidity of barium sulfate sols, as measured by the nephelometer, was different for particles of the same size formed in glycerin-water and glycerin-alcohol mixtures. The difference in reading is probably due to the variation in crystalline forms and in the refractive indices of the salt thrown down in the different media. The turbidity in such mixtures is a maximum with particles around $200\mu\mu$ in reflected light and around $1000\mu\mu$ in transmitted light.

Svedberg and Nichols² investigated the size and distribution of size of particles by a centrifugal method for a barium sulfate sol prepared by the interaction of $N/10$ barium thiocyanate and $N/10$ ammonium sulfate in the presence of potassium citrate.

COLLOIDAL SULFATES OF STRONTIUM AND LEAD

Colloidal Strontium Sulfate.—Strontium sulfate, which is soluble in water to the extent of 1.48 grams per liter at 20° , cannot be precipitated in the colloidal state from aqueous solution. Since the solubility of the salt is much less in aqueous alcohol than in water, von Weimarn³ obtained it in the gel form by precipitation from alcoholic solutions.

Odén and Werner⁴ studied the mechanism of the precipitation of strontium sulfate by measuring the conductivity of the solu-

¹ *Kolloid-Z.*, **32**, 73 (1923).

² *J. Am. Chem. Soc.*, **45**, 2910 (1913); cf., also, NICHOLS and LIEBE: Colloid Symposium Monograph, **3**, 268 (1925).

³ *Kolloid-Z.*, **2**, 76 (1907).

⁴ *Arkiv. Kemi, Mineral. Geol.*, **9**, No. 32 (1926); *Chem. Abstr.*, **21**, 570 (1927).

tions resulting from mixing measured amounts of strontium hydroxide and sulfuric acid. The conductivity of the solution supersaturated with respect to the precipitate was found to be constant at first for a considerable period of time, the length of which was determined by the concentration of the base and acid. After this interval, the conductivity decreased gradually during the process of actual precipitation until it reached a minimum value corresponding to complete precipitation. This process required several hours in concentrations of 0.02 to 0.06 normal but only a few minutes in more concentrated solutions. It was found that the rate of growth of single crystals (primary particles) in a supersaturated solution and in a non-aggregated state may be expressed by the equation $V_k = K \cdot O_t \cdot (C_t - C_m)$ where V_k is the velocity of crystallization; O_t the total surface of the crystals at time t ; C_t and C_m concentration of the solution at time t and at saturation, respectively; and K a constant.

Colloidal Lead Sulfate.—Lead sulfate is much less soluble in water (0.041 gram per liter at 20°) than the strontium salt but it cannot be thrown down as a transparent gel like the more insoluble barium sulfate. Contrary to what one might expect, however, Buchner and Kalff¹ mixed equivalent amounts of soluble lead salt and alkali sulfate and obtained a lead sulfate sol similar to von Weimarn's barium sulfate sol thrown down from 3 normal solutions.² Lead sulfate sol formed in the absence of protective colloids flocculates in a short time; but Leuze³ prepared a stable sol by treating a mixed solution of lead acetate, sodium hydroxide, and sodium protalbinate, so-called, with a solution of sodium sulfate. On dialysis the brown sol which was first formed became gradually opalescent and milky.

¹ *Rec. trav. chim.*, **39**, 135 (1920).

² Cf. p. 6.

³ "Zur Kenntnis kolloidaler Metalle und ihrer Verbindungen," Erlangen, 21 (1904).

CHAPTER XII

GYPSUM—PLASTER OF PARIS

Calcium sulfate exists in three chemical forms: the dihydrate, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$; the hemihydrate, $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$; and the anhydrous salt. The dihydrate and the anhydrous salt occur in nature, the former as gypsum and the latter as anhydrite. The hemihydrate does not occur in nature but may be prepared by heating gypsum under suitable conditions. The manufactured compound known as plaster of paris or calcined gypsum possesses hydraulic properties and is largely employed in preparing wall plaster, for ornamental plaster work, for making plaster casts, and as a cement. Dehydration of gypsum at elevated temperatures, under suitable conditions, yields an anhydrous product which likewise possesses hydraulic properties but, unlike plaster of paris, the rate of setting is usually quite slow. This anhydrous salt is a constituent of the hard plaster used for flooring and of most of the Grecian and mediaeval plaster cements. Keene's cement and Estrich gypsum (flooring plaster) are examples of cements consisting essentially of anhydrous calcium sulfate.

THE SYSTEM CALCIUM SULFATE—WATER

Gypsum is the stable form of calcium sulfate under ordinary conditions of temperature and in contact with moist air but the hemihydrate and anhydrite often exist as metastable forms under these conditions because of the slowness of the transformation to gypsum. Van't Hoff¹ found the inversion point for gypsum and plaster of paris to be 107° and 971 millimeters; and for gypsum and insoluble anhydrite to be 635° and 175 millimeters. The transformation to the anhydrous salt may be effected at as low a temperature as 30° in contact with a solution of sodium chloride. Complete dehydration results by heating for 24 hours

¹ VAN'T HOFF, ARMSTRONG, HINRICHSEN, WEIGERT, and JUST: *Z. physik. Chem.*, **45**, 257 (1903).

at $97^\circ \pm 2^\circ$ in a current of air in which the aqueous tension is 23 millimeters.¹

To prepare plaster of paris, the gypsum may be burned in ordinary air at a temperature only slightly in excess of 107° but in actual practice a higher temperature is employed, mainly because the dehydration velocity is too small just above the transition point. From a survey of the literature on the burning of gypsum² it appears that the American practice is to use a temperature of 175 to 200° because it is believed that complete dehydration takes place only above 200° ,³ whereas the Germans burn at about 130° to prevent the formation of anhydrous calcium sulfate above this temperature.⁴ The English apparently burn at 110 to 120° ,⁵ although admitting that the temperature may be raised to 200° before anhydrous calcium sulfate is formed. Bancroft has reconciled these discrepant statements by taking the time factor into account. Since gypsum loses water more rapidly at 200° than at 130° , the heating period must be shorter in the former case to burn to the same end point, provided the kilns are otherwise the same. This has been found to be the case in Bancroft's laboratory⁶ and has been substantiated by Hursch's⁷ statement that "commercially, temperatures up to 200° or above are used but for short periods of time." The best temperatures for commercial burning will vary with the cost of fuel, the size and nature of the plant, etc. The quality of the product will doubtless vary with the temperature of formation but the author is not aware of any data which bear on this question.

Van't Hoff⁸ demonstrated further, that gypsum in the presence of water may be converted into anhydrous calcium sulfate which differs from natural anhydrite in being fairly soluble in water and in setting even more rapidly than plaster of paris. This so-called soluble anhydrite is produced when precipitated gypsum is

¹ BALAREW: *Z.anorg. Chem.*, **156**, 258 (1926); cf. LINCK and JUNG: *Ibid.*, **137**, 407 (1924).

² KEANE: *J. Phys. Chem.*, **20**, 701 (1916).

³ ECKEL: "Cements, Limes, and Plasters," 31 (1905).

⁴ ROHLLAND: *Z. anorg. Chem.*, **31**, 437 (1902); **35**, 194; **36**, 332 (1903).

⁵ DESCH: "The Chemistry and Testing of Cement," 48 (1911).

⁶ KEANE: *J. Phys. Chem.*, **20**, 701 (1916).

⁷ *Trans. Am. Ceram. Soc.*, **17**, 549 (1905).

⁸ *Z. physik. Chem.*, **45**, 257 (1903).

heated in *vacuo* over sulfuric acid between 60 and 90°; when gypsum regenerated from plaster of paris is heated at 100°; or from any form of gypsum or the hemihydrate heated at 180°. Davis¹ obtained the soluble anhydrite by heating ordinary gypsum at 107 to 108°.² In addition to the soluble and insoluble anhydrite, Rohland³ believes that three anhydrous forms of calcium sulfate exist: α CaSO_4 , which forms between 130 and 525° and which takes up water but does not set; β CaSO_4 which is formed at 525° and which takes up water and hardens; and γ CaSO_4 which is formed above 600° and which does not hydrate or harden. There is, however, no satisfactory evidence for inversion points at 130 and 525° and it is not likely that any exist. Thus, Rohland's β CaSO_4 , which he claims to get only between 525 and 600°, is the flooring plaster or Estrich gypsum which Müller⁴ says is best formed at 800 to 900°. Similarly, Glasenapp⁵ claims that gypsum burned up to 400° will harden; but that burned between 400 and 800° will not hydrate or harden, while above 800° Estrich gypsum is formed. He recommends, therefore, 900° or higher as the best temperature for preparing the commercial product. Van't Hoff and Just⁶ calcined a sample of gypsum at 200° for 10 hours and found 92 per cent of it to set in 23.5 hours while in a sample calcined at 300° for 10 hours, only 56 per cent had set in 21 hours. Again, 67 per cent of a sample of commercial flooring plaster had set in 13 days while only 39 per cent of a similar sample calcined 10 hours at 400° had set in the same time.

It thus appears that the non-setting variety of calcium sulfate, insoluble anhydrite, can be obtained at a temperature as low as 30° and it can also be formed under suitable conditions at any other temperature up to 1000°. Anhydrite which sets with water can likewise be obtained at any temperature between 60 and

¹ *J. Soc. Chem. Ind.*, **26**, 727 (1907).

² In a private note J. A. Miller questions whether Davis obtained soluble anhydrite at as low a temperature as 107° in the absence of a dehydrating agent.

³ *Z. anorg. Chem.*, **31**, 437 (1902); **35**, 194; **36**, 332 (1903).

⁴ Cf. HURSCH: *Trans. Am. Ceram. Soc.*, **17**, 549 (1905).

⁵ *Z. angew. Chem.*, **27**, III, 308 (1914).

⁶ *Sitzb. Preuss. Akad. Wiss.*, 249 (1903); VAN'T HOFF, ARMSTRONG, HINRICHSEN, WEIGERT, and JUST: *Z. Physik. Chem.*, **45**, 303 (1903).

1000° provided the heating is done in a suitable way. Since there is apparently no inversion point from the soluble to the insoluble form, and since it is possible to obtain all varieties from an anhydrous salt which sets more rapidly than plaster of paris to an anhydrous salt which does not take up water at all in a reasonable time, it is probable that there is but one modification of the anhydrous salt, the observed variation in properties being due to a difference in the size and physical character of the particles. In support of this view Keane¹ showed that gypsum calcined at 600° behaved like dead-burned plaster when the particles were 0.05 millimeter in diameter but when the particle size was reduced to 0.005 millimeter in diameter by grinding, the product set quite rapidly to a hard resistant mass.² Even natural anhydrite will set if ground sufficiently fine. Thus Gill³ found that both finely ground anhydrite and rough lumps of dead-burned plaster of paris were bound firmly together by gypsum crystals after standing covered with water for 6 years. Microscopic examination of a plaster burned at 750° revealed a granular state which Budnikov⁴ tacitly assumed to indicate a rearrangement in the molecular structure of the calcium sulfate. It is unfortunate that Budnikov did not test the accuracy of this deduction by submitting the alleged isomeric forms to x-ray analysis.

In this connection, attention should be called to a slow-setting variety of hemihydrate formed by the prolonged action on gypsum of boiling water⁵ or of water at 130 to 150°.⁶ Davis⁶ suggests that this slow-setting product may be another modification of hemihydrate which bears the same relation to the fast-setting variety that slow-setting anhydrite does to rapid-setting anhydrite. Since the conditions of preparing slow-setting hemihydrate favor the formation of relatively large dense par-

¹ *J. Phys. Chem.*, **20**, 701 (1916); cf., also, WINTERBOTTOM: *Bull. S. Australian Dept. Chem.*, **7** (1917).

² Cf., also, HARTNER: *Z. angew. Chem.*, **33**, I, 175 (1920); WEISSENBERGER: *Kolloid-Z.*, **32**, 181 (1923).

³ *J. Am. Ceram. Soc.*, **1**, 65 (1918).

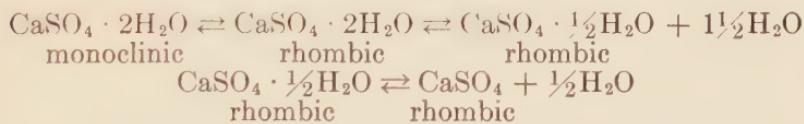
⁴ *Z. anorg. Chem.*, **159**, 87 (1926).

⁵ DAVIS: *J. Soc. Chem. Ind.*, **26**, 733 (1907).

⁶ LECHATELIER: "Recherches expérimentales sur la constitution des mortier hydrauliques," Paris (1887).

ties, it is probable that the variation in properties of the two hemihydrates, like that of the anhydrous salt, is attributable to a difference in the physical character of the particles.

The stable form of gypsum under ordinary conditions is monoclinic but Davis¹ believes that it changes into the rhombic form before it is dehydrated by heating. In support of this view, it is demonstrated that water is not lost immediately on heating² but, instead, there is a period of induction which is probably caused by the transformation to the rhombic modification. Moreover, the optical properties of gypsum crystals are altered by heating. At the ordinary temperatures, the optic axes of the salt lie in the plane of symmetry of the crystal but on heating to a temperature above 91° and before dehydration begins, they revolve so as to take up a position at right angles to this plane. The formation of rhombic crystals actually has been observed by Lacroix³ on heating a plate of gypsum. Finally, it is pointed out that all the products of dehydration of gypsum are orthorombic in symmetry and that the dehydration of the hemihydrate, which is unattended by any change of system, manifests no period of induction. The transformation from monoclinic gypsum to the anhydrous salt is believed to be completely reversible, rhombic gypsum and hemihydrate being intermediate products. The process may be represented by the equations:



THE SETTING OF PLASTER OF PARIS

The setting of plaster of paris involves a definite chemical transformation from the hemihydrate to the dihydrate of calcium sulfate. Since the former is more than five times as soluble as the latter⁴ at room temperature, the following mechanism of the

¹ *J. Soc. Chem. Ind.*, **26**, 727 (1907).

² Cf. SHENSTONE and CUNDALL: *J. Chem. Soc.*, **53**, 544 (1888).

³ *Compt. rend.*, **126**, 360, 553 (1898).

⁴ MARIGNAC: *Arch. sci. phys. nat.*, **48**, 120 (1873). While the ratio of the solubilities of plaster of paris and gypsum are large, the absolute solubilities are relatively small, 1.2 and 0.2 per cent, respectively, at 18°.

setting process was outlined by LeChatelier:¹ The hemihydrate first forms a saturated solution in water, then hydrates to the dihydrate giving a supersaturated solution of the latter from which is deposited a compact mass of interlacing needle-shaped crystals—the set plaster.² The quantity of water sufficient to bring the hemihydrate back to the fully hydrated condition

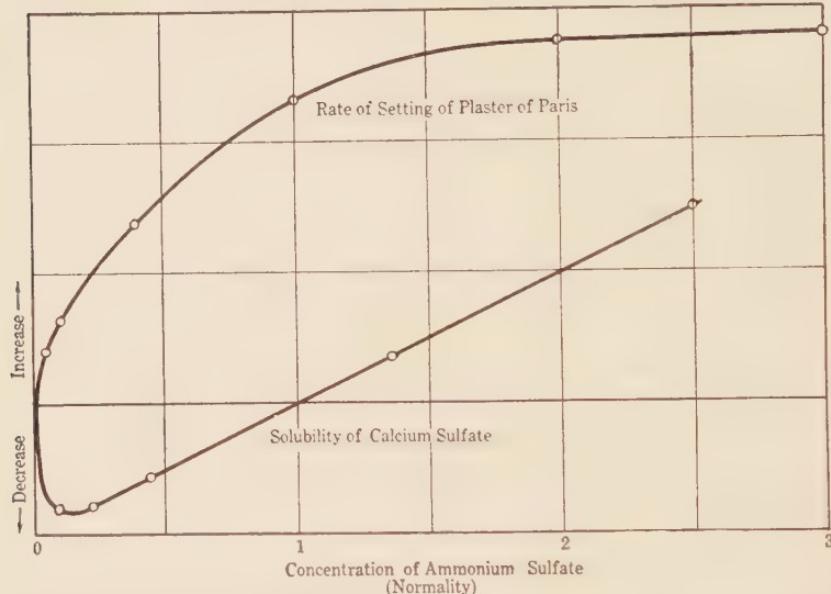


FIG. 19.—Influence of ammonium sulfate on the rate of setting of plaster of paris and on the solubility of calcium sulfate.

is very much less than is necessary to dissolve it; but complete crystallization is accomplished, nevertheless, in accord with the following mechanism: the hemihydrate readily forms a solution supersaturated with respect to the dihydrate from which the latter deposits, thereby releasing the water which dissolves another portion of the hemihydrate, the process continuing indefinitely until the transformation is complete. The importance of using a limited quantity of water is accounted for on

¹ "Recherches expérimentales sur la constitution des mortier hydrauliques," Paris (1887); cf., also, VAN'T HOFF *et al.*: *Z. physik. Chem.*, **45**, 257 (1903); ROHLAND: *Z. anorg. Chem.*, **31**, 437 (1902); **35**, 194; **36**, 332 (1903); JOLIBOIS and CHASSEVENT: *Compt. rend.*, **177**, 113 (1923).

² Cf., also, CHASSEVENT: *Ann. chim.*, **6**, 244 (1926).

the grounds that the crystallization must take place from a strongly supersaturated solution. If a large excess of water is employed, the hydration takes place quite readily but the crystals separating from the comparatively dilute solutions are an incoherent mass of prisms.

While this classical theory of the setting has long been considered satisfactory, there are still a number of points which it does not explain adequately. Thus it is known that soluble salts may have a marked effect on the rate of setting of plaster,¹ some salts accelerating the time of set and others retarding it. To account for this behavior Rohland² assumes, in accord with LeChatelier's theory, that any salt which increases the solubility of calcium sulfate will accelerate the setting, while substances which decrease the solubility will retard the setting. Neville³ points out that this explanation is unsatisfactory since the solubility of calcium sulfate is decreased by small amounts of practically all soluble sulfates, yet these exert a marked accelerating effect upon the setting of plaster of paris. This is illustrated in Fig. 19, which shows the absence of any relationship between the effect of ammonium sulfate on the solubility of calcium sulfate and its effect on the rate of setting of plaster.⁴ Furthermore, the formation of a felt of needle crystals⁵ is, in itself, insufficient to account for the properties of the set plaster. Thus a solution of gypsum may be precipitated by alcohol in such a way that a dense felt of crystal needles results but the dried mass is altogether unlike set plaster in physical properties.⁶ Glasenapp's assumption that the hardness of set plaster results from the growing together of the crystals was disproven by Wolfgang Ostwald,⁷ who showed that the clusters of crystals readily observed at thousandfold magnification, consist of relatively dense individual crystals which have not grown together and

¹ DITTE: *Compt. rend.*, **126**, 694 (1898); WELCH: *J. Am. Ceram. Soc.*, **6**, 1197 (1923).

² *Z. Elektrochem.*, **14**, 421 (1908).

³ *J. Phys. Chem.*, **30**, 1037 (1926).

⁴ CHASSEVENT: *Ann. chim.*, **6**, 313 (1926).

⁵ MOYE: "Der Gyps," Leipzig, 32 (1906); LECHATELIER: *Compt. rend.*, **96**, 717 (1883); GLASENAPP: *Tonind. Ztg.*, **32**, 1148, 1197, 1230 (1908).

⁶ OSTWALD: "Lehrbuch Allgemeinen Chemie," 2nd ed., **2**, 769 (1911).

⁷ Cf. OSTWALD and WOLSKI: *Kolloid-Z.*, **27**, 79 (1920).

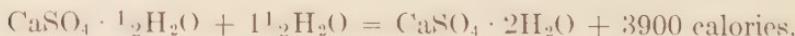
show no secondary ramifications. It appears, therefore, that the way in which the needle crystals are laid down is of fundamental importance.

More recent considerations indicate that colloidal processes are of importance in the setting of plaster of paris as they are in the setting of portland and aluminous cements.¹ Thus Cavazzi² and Traube,³ for independent reasons, suggest that the setting of plaster consists in the initial formation of a gel which gradually changes into needle-shaped crystals of gypsum. Cavazzi bases his suggestion on the observation that gypsum can be precipitated by alcohol under certain conditions, giving a gel in which small crystal needles are subsequently formed.

It is of interest in this connection that calcium sulfate gel played an important role in biology until comparatively recently. Mud dredged from the ocean and preserved in alcohol was found to contain a gelatinous substance which was believed to exist in great masses in the depths of the ocean and to consist of undifferentiated protoplasm. Regarding it as an organism which represented the simplest form of life, Huxley, in 1868, named it *Bathybius* ($\beta\alpha\theta\bar{\nu}$ s deep, $\beta\iota\sigma$ s life). About 30 years ago Möbius showed that this *Bathybius* was nothing more or less than calcium sulfate gel precipitated by alcohol added to the muddy sea water.

Traube observed the effect of salts on the time required for plaster of paris to attain a definite state of hardness. He found cations to be especially important in accelerating the set, the order of influence being the reverse of that in which they precipitate sols, thus indicating that colloidal phenomena are concerned in the setting process. Measurements of change of viscosity of dilute plaster of paris suspension with time⁴ indicate a similarity in the behavior of plaster of paris and gelatin.

Since the hydration of plaster of paris is an exothermal reaction,



¹ See WEISER: "The Hydrous Oxides," 382 (1926).

² *Gazz. chim. ital.*, **42**, (2) 626 (1912); *Kolloid-Z.*, **12**, 196 (1913).

³ *Kolloid-Z.*, **25**, 62 (1919).

⁴ OSTWALD and WOLSKI: *Kolloid-Z.*, **27**, 78 (1920).

Neville¹ was able to follow the setting process thermometrically. The method was as follows: Forty grams of a high grade commercial plaster of paris were mixed with 30 to 120 cubic centimeters of water or a solution, stirred for a definite length of time in a paper cup which was then placed in a calorimeter, and the rise in temperature noted at short intervals as the setting process took place. In Fig. 20 are given the reaction curves for a mixture of 40 grams of plaster with 30 cubic centimeters of water;

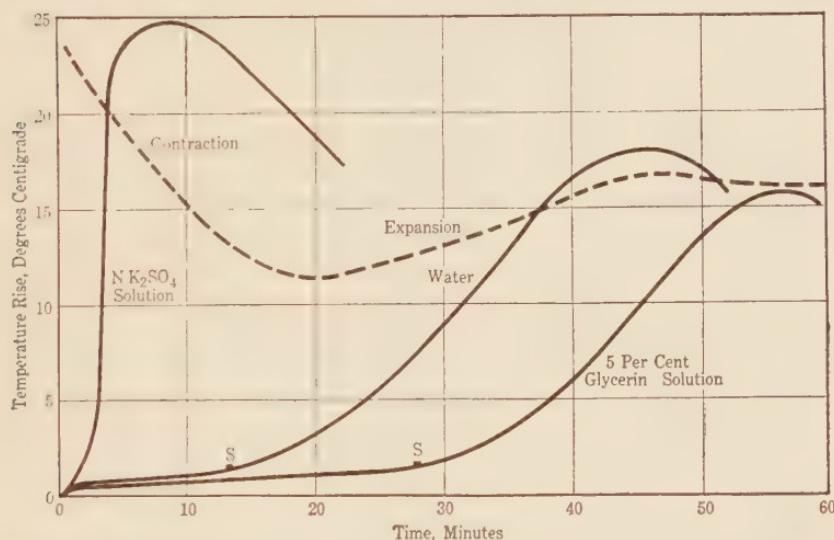


FIG. 20.—Time-temperature curves for the setting of plaster of paris. (Broken line represents the volume change for water-plaster of paris.)

for a similar mixture accelerated by potassium sulfate and for one retarded by glycerin.

When the plaster and water were thoroughly stirred for a short time in the above proportions, a thin paste or cream resulted which was readily poured into molds. There was a slight rise in temperature at this point—usually less than 1° —due to the heat of wetting or adsorption. After standing 6 minutes, the mixture would not pour. When 40 grams of plaster were mixed with 30 cubic centimeters of normal potassium sulfate, the mixture became stiff in $\frac{1}{2}$ minute. A $\frac{1}{2}$ -minute interval of stirring was therefore used in all experiments. The points marked *S* on the

¹ *J. Phys. Chem.*, **30**, 1037 (1926).

curves correspond to the initial set stage. At this point, the plaster was perfectly rigid and appeared dry. The broken curve represents the volume change with time corresponding to the time curve labelled "water."

These observations of Neville throw considerable light on the mechanism of the setting process. Since the point *S*, corresponding to the initial set, is on the flat portion of the curve before the evolution of heat has begun, the hydration of plaster of paris to gypsum cannot have occurred to any appreciable extent. It follows, therefore, that the initial set is not due to chemical combination of the plaster with water but to adsorption of water with the formation of a gel. This conclusion is supported by the time-volume curve. The initial concentration is apparently due to adsorption of water and the subsequent expansion to the formation of gypsum crystals. The setting is thus a two-stage process. In the first stage, the forces of adsorption bring the plaster of paris and water into the sphere of chemical action in the form of a gel; and in the second stage, chemical forces effect a reaction between the two substances to form gypsum, crystals of which of necessity interlace and anastomose throughout the material giving a coherent mass. An approximate determination of the heat evolved shows that practically all of the plaster has reacted at the time corresponding to the maximum temperature reached.

Contrary to Neville's view, Davis¹ attributes the initial contraction to the formation of instable rhombic gypsum and the subsequent expansion to the transformation to monoclinic crystals. While this may be a contributing factor in the volume changes accompanying the setting of plaster, it is apparently not the only factor and probably not the most important one. Thus it will be seen from Neville's curves that the initial contraction approaches the minimum value before there is any marked evolution of heat, indicating that there is a marked contraction without any gypsum being formed at all. One may get around this objection to Davis' view by assuming that the heat evolved in the hydration of plaster of paris to monoclinic gypsum arises for the most part from the transformation of the rhombic to the monoclinic form of the dihydrate. This hypothesis appears

¹ *J. Soc. Chem. Ind.*, **26**, 727 (1907).

improbable, however, since Davis showed that heat must be applied continuously to effect dehydration following the initial period of induction which corresponds to the transformation from the monoclinic to the rhombic form.

The effect of salts on the setting of plaster of paris is well illustrated by Neville's observations of the time corresponding to the maximum rise in temperature when 40 grams of plaster of paris are stirred 15 seconds with 30 cubic centimeters of water or a solution. The values recorded in Table XXXIV are reproducible within 30 seconds. The data confirm Traube's conclusion that the accelerating action of a salt is due to the cation modified to some extent by the anion. The order of the alkali metals in accelerating the setting is: K > NH₄ > Na > Li. This is the same as that observed in the coagulation of a negative sol such as arsenic trisulfide. The anions apparently limit the activity of the cations to some extent. Considered as retarders, the order of the monovalent anions is the usual one: I > NO₃ > Br

TABLE XXXIV.—EFFECT OF SALTS ON THE SETTING OF PLASTER OF PARIS

Reagent	Time corresponding to maximum rise in temperature, minutes	Reagent	Time corresponding to maximum rise in temperature, minutes
Pure water.....	44.0	N Na ₂ SO ₄	12.5
N HCl.....	18.0	N (NH ₄) ₂ SO ₄	6.0
N LiCl.....	19.0	N CuSO ₄	12.0
N NaCl.....	12.0	N MgSO ₄	20.0
N NH ₄ Cl.....	10.5	N ZnSO ₄	12.0
N KCl.....	6.0	N Al ₂ (SO ₄) ₃	25.0
N KBr.....	6.5	Saturated CaSO ₄	44.5
N KI.....	8.5	Saturated H ₂ BO ₃	63.0
N KNO ₃	7.0	Saturated NaCl....	180.0
N K ₂ SO ₄	7.5	Saturated Na ₂ B ₄ O ₇ .	3 days

> Cl. Contrary to what one might expect from colloid chemical considerations, the accelerating action of aluminum and magnesium salts is less than that of the alkali salts. The exact role of the accelerating ions is not clear but apparently they serve both

to speed up the adsorption of water to form the gel and subsequently to catalyze the chemical reaction between hemihydrate and water. This is but another way of saying that the mechanism of the accelerating action of some salts is not known. Such salts as borax and saturated sodium chloride retard the setting of plaster by preventing gel formation. In these cases, the setting process is one of solution, hydration, and crystallization only; and the set mass resulting from the slow process is composed of large crystals and is crumbly.

The addition of small amounts of substances such as gelatin and glue retard the setting by interfering with the formation of crystals while larger amounts completely inhibit crystal formation and so prevent the setting.¹ It is said that the ancient Romans used blood to retard the setting of plaster of paris. Any protective colloid which is strongly adsorbed by gypsum will tend to inhibit its crystallization and so delay or prevent the setting of the plaster.

The utility of plaster of paris in the preparation of casts depends on its power of filling the mold by its expansion on setting and so taking a sharp impression of its surface. Although there is an expansion, the final volume of the crystallized gypsum is less than the sum of the original volumes of the materials by about 7 per cent as can be calculated from the respective densities of the substances concerned.² The apparent density of a plaster cast is, however, less than that of the plaster and water constituting it since the mass is porous, being made up of groups of interlocking crystals with spaces between them. The manner in which the crystals are laid down is probably a more important factor in filling the mold than is the change from the rhombic to the monoclinic form which is assumed to be less dense.³

The initial contraction and subsequent expansion of plaster was apparently well known in Persia for up to about 1880 this property was utilized as a means of executing criminals.⁴ The condemned individuals were placed in hollow stone columns and

¹ OSTWALD and WOLSKI: *Kolloid-Z.*, **27**, 78 (1920); TRAUBE: *Kolloid-Z.*, **25**, 62 (1919).

² DESCH: "The Chemistry and Testing of Cement," 105, 108 (1911).

³ KEANE: *J. Phys. Chem.*, **20**, 721 (1916).

⁴ FRISWELL: *J. Soc. Chem. Ind.*, **26**, 737 (1907).

surrounded with wet plaster of paris. At first they suffered but little inconvenience, but after a time they showed signs of distress and screamed loudly; finally, paralysis and death supervened. This doubtless occurred as the expansion of the plaster compressed the thorax and abdomen.

III
COLLOIDAL HALIDES

CHAPTER XIII

THE COLLOIDAL HALIDES OF SILVER, LEAD, AND MERCURY

THE COLLOIDAL HALIDES OF SILVER

The silver halides with the exception of silver fluoride are quite insoluble; hence, on mixing aqueous solutions of silver salts and alkali halides, they precipitate in flocculent masses composed of very minute crystals.¹ The physical character of the gels vary widely with the conditions of precipitation.² The presence of certain salts during precipitation has a marked effect on the physical character and properties of the halides. Thus Lüppo-Cramer³ found that a small amount of lead bromide or cadmium bromide gives a silver bromide which is more voluminous, whiter, and more stable to light than when the lead or cadmium salt is absent. Moreover, lead bromide is said to bleach a silver bromide darkened by light although colloidal silver alone is not brominated by this salt. Lead chloride and both mercuric and mercurous chloride have similar effects on the gel structure of silver chloride. Zinc, copper, iron, and uranium salts have no apparent effect on the halides. Lüppo-Cramer's qualitative observations should be confirmed and a quantitative study made of the role played by the salts in altering the physical character and properties of silver halide gels.⁴

The curdy precipitate formed on mixing silver nitrate with alkali halide is white with the chloride, greenish white with the bromide, and pale yellow with the iodide. The solubilities in mols per liter are as follows: AgCl, 1.25×10^{-5} ; AgBr, 6.60×10^{-7} ; and AgI, 9.7×10^{-9} , the chloride being almost twenty times as soluble as the bromide and the bromide almost seventy

¹ BÖHM and NICLASSEN: *Z. anorg. Chem.*, **132**, 1 (1924).

² LIESEGANG: *Phot. Chronik.*, **16**, 219 (1909).

³ *Kolloid-Z.*, **5**, 103 (1909).

⁴ Cf. WEISER: *J. Phys. Chem.*, **20**, 640 (1916); **21**, 314 (1917).

times as soluble as the iodide. Since the silver halides follow the usual rule that the most insoluble salt precipitates in the most finely divided form, the stability of the halide sols is in the order $\text{AgI} > \text{AgBr} > \text{AgCl}$. Lottermoser¹ first called attention to the fact that sols are formed on mixing dilute solutions containing silver ions and halide ions provided one or the other is present in excess. If silver ions are in excess, the colloidal particles are positively charged and if iodide ions are in excess, the particles are negatively charged. Thus,² if $N/10$ silver nitrate is allowed to drop from a burette into 500 cubic centimeters of $N/500$ silver

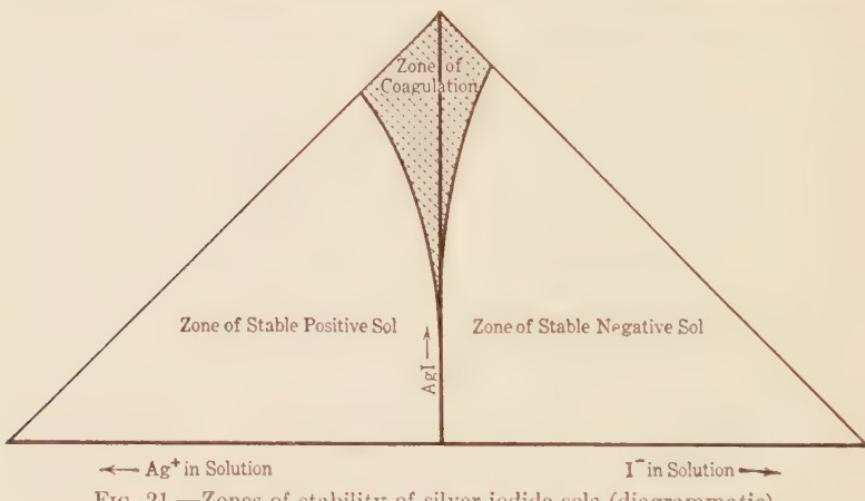


FIG. 21.—Zones of stability of silver iodide sols (diagrammatic).

nitrate solution stirred by a motor stirrer, the first drop gives a yellow-green, perfectly transparent sol which becomes gradually more and more opalescent with further additions of iodide until at approximately the equivalence point between iodide and silver, the opalescence increases rapidly, the solution becoming cloudy, whereupon an additional drop of the silver nitrate solution causes flocculation of the silver iodide. If the process is reversed and $N/10$ potassium iodide is allowed to drop slowly into $N/250$ silver nitrate, the phenomenon is similar except that clouding takes place somewhat more rapidly. These facts may be represented diagrammatically as in Fig. 21. On the right is the zone of

¹ *J. prakt. Chem.*, [2] **72**, 39 (1905).

² LOTTERMOSER, SEIFERT, and FORSTMANN: *Kolloid-Z.*, (Zsigmondy Festschrift), **36**, 230 (1925).

stability of the negative sol formed by adding silver nitrate slowly to potassium iodide solution and on the left, the zone of stability of the negative sol formed by the reverse procedure. On either side of the perpendicular line which represents equivalent amounts of Ag^+ and I^- ions, is a shaded portion, the zone of flocculation. This is wider on the left since the positive sol is less stable than the negative. Similar relationships obtain with the closely related silver cyanide and silver thiocyanate.

Since the negative halide sols are readily coagulated by multivalent cations and the positive sols by multivalent anions, the stability of sols is much less if the interacting solutions contain a multivalent ion opposite in charge to the stabilizing ion. Thus a negative sol can be formed by adding $N/20$ silver nitrate to $N/20$ potassium iodide solution, whereas, if barium iodide or cadmium iodide is used instead of the potassium salt, the solutions must be at least as dilute as $N/100$ or sol formation does not occur.¹

That the negatively charged halide sols are more stable than the positive sols is evidenced by the following observations on silver iodide: The positive sol is more cloudy and settles out more rapidly than the negative in the presence of a like excess of the stabilizing ions; the positive sol cannot be purified by dialysis without agglomeration, whereas the negative sol can be purified to a certain extent in this way; finally, a freshly precipitated gel of silver iodide is peptized in part by shaking with a dilute potassium iodide solution while silver nitrate does not peptize the precipitated gel.

Sheppard and Lambert² studied the relative peptizing power of different electrolytes on potassium bromide formed in the presence of a slight excess of silver ion. Potassium chloride was found to disperse the gel equally as well as potassium bromide but the peptizing power of potassium iodide was considerably less. Ammonium bromide and hydrobromic acid have the same peptizing power but fall far short of the chloride and bromide of potassium in this respect. Nitric acid, ammonium hydroxide, and potassium hydroxide have no peptizing action and

¹ LOTTERMOSER: *Kolloid-Z.*, **2**, Supplement I, p. IV (1907).

² Colloid Symposium Monograph, **4**, 281 (1926).

their presence cuts down the peptizing action of potassium bromide.

The precipitation of silver halides in the absence of an excess of either positive or negative ions, is regarded by Lottermoser as due to coagulation of the particles into larger secondary aggregates which settle out. Jableczynski¹ objects to this mechanism of the precipitation on the ground that it does not explain the velocity of increase of turbidity in the presence of gelatin or other protective colloids which inhibit precipitation even in low concentrations. The view held by Jableczynski is that the formation of a precipitate and the process of grain growth, both in the presence and absence of gelatin, is entirely a process of recrystallization by solution of the smaller grains and growth of larger ones at their expense (Ostwald ripening) until the larger grains are thrown down. This contention of Jableczynski is contradicted by Sheppard and Lambert's² observations of reversible flocculation and deflocculation of a part of the silver halides precipitated in the absence of gelatin, and by microscopic examination which reveals the presence of secondary aggregates consisting of loosely adhering primary particles. In the absence of protective colloids, it thus appears that aggregation is the important factor in causing precipitation, although some recrystallization does take place; while in the presence of protective colloids, the coagulation is largely inhibited at least until high concentrations of the reactants are used. The grain growth observed in the ripening of photographic emulsions is due primarily to a process of recrystallization from solution in which crystal aggregation plays but a minor role.³

Jableczynski⁴ studied the velocity of coagulation of silver halide sols, both in the presence and the absence of protective colloids, and found the process to take place in accord with Smoluchowski's theory of rapid coagulation.⁵ This furnishes no evidence as to whether the precipitation is due primarily to aggregation of primary particles or to recrystallization, since both processes

¹ JABLCZYNSKI, FORDONSKI, FRANKOWSKI, LISIEKI, and KLEIN: *Bull. soc. chim.*, **33**, 1392 (1923).

² Colloid Symposium Monograph, **4**, 281 (1926).

³ SHEPPARD: Colloid Symposium Monograph, **1**, 346 (1923).

⁴ *Bull. soc. chim.*, **35**, 1286 (1924).

⁵ See p. 29.

follow at first the same law for the diminution of number of particles.¹

Silver halide sols prepared by Lottermoser's method are not very stable at best. To stabilize them Lobry de Bruyn² used gelatin and Paal and Voss³ the so-called lysalbinic acid or its sodium salt. Paal's preparations were very stable, the addition to them of five volumes of saturated sodium chloride solution or an equal amount of 10 per cent sodium phosphate solution causing no precipitation. An excess of 10 per cent calcium chloride caused clouding but no precipitation, even on heating. Gutbier⁴ prepared fairly stable silver halide sols by treating with the respective halogens, a silver sol prepared by reduction of silver nitrate with hydrazine hydrate in the presence of gum arabic. Von Weimarn⁵ used caoutchouc as a protective colloid for preparing silver halide sols in aromatic hydrocarbons.

ADSORPTION BY SILVER HALIDES

Since the positive and negative silver iodide sols owe their stability to preferential adsorption of silver and iodide ions, respectively, it follows that the greater stability of the negative sol is due to stronger adsorption of iodide ions than of silver ions by the silver iodide. This is borne out by some observations of Lottermoser and Rothe⁶ on the adsorption by silver iodide of potassium iodide and silver nitrate, respectively, as shown in Fig. 22. It will be seen that the maximum adsorption of the iodide by silver iodide is considerably greater than that of silver nitrate at the same concentration. The maximum in the adsorption isotherm of potassium iodide is due to a distinct change in the physical character of the silver iodide gel in the presence of the larger amounts of potassium salt.⁷

It has been recognized for a long time that an insoluble salt shows a strong preferential adsorption for its own ions. Thus,

¹ SHEPPARD and LAMBERT: Colloid Symposium Monograph, **4**, 281 (1926).

² Rec. trav. chim., **19**, 251 (1900).

³ Ber., **37**, 3862 (1904).

⁴ Kolloid-Z., **4**, 308 (1909).

⁵ J. Russ. Phys. Chem. Soc., **48**, 1046 (1916).

⁶ Z. physik. Chem., **62**, 359 (1908).

⁷ Compare with the behavior of cadmium sulfide in the presence of hydrochloric acid (p. 91).

barium sulfate adsorbs both barium ion and sulfate ion strongly, the silver halides adsorb both silver and the halide ions strongly, and the hydrous oxides adsorb the heavy metal cations and hydroxyl ion strongly. This relatively strong adsorption of a common ion is probably due to the fact that it fits into the crystal lattice of the adsorbent. From this point of view, the adsorption force in such cases is identical with the cohesive force of the

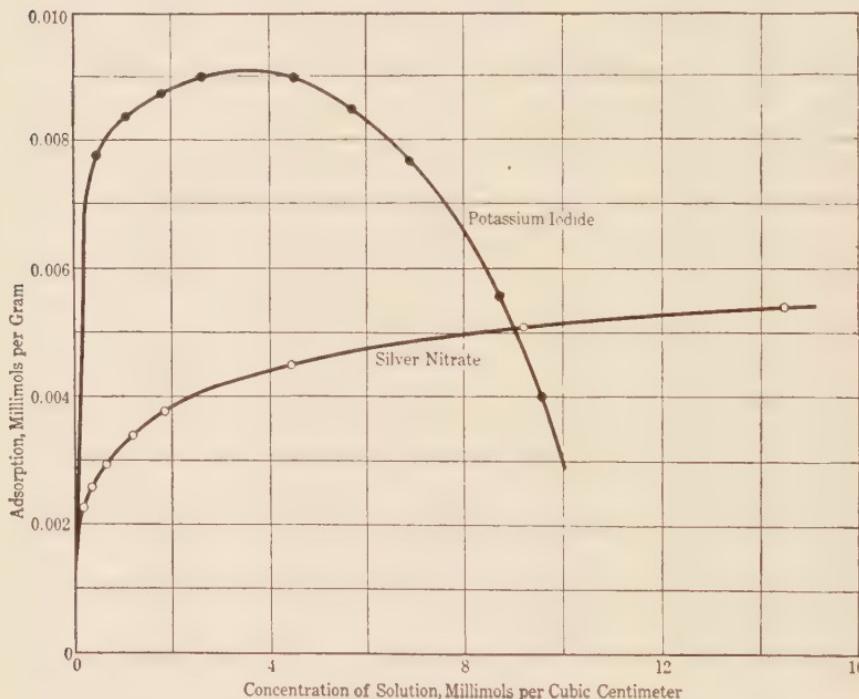


FIG. 22.—Adsorption of potassium iodide and of silver nitrate by silver iodide.

adsorbent so that the adsorption process may be considered to be comparable in certain respect to the growth of crystals in a saturated solution. In line with this, Paneth¹ and Horovitz² observed that radium is strongly adsorbed by barium sulfate and barium chromate, whereas it is not adsorbed at all by hydrous chromic oxide or silver chloride. Since radium sulfate and radium chromate are insoluble compounds and radium oxide and radium chloride are not, Paneth was led to conclude that

¹ *Physik. Z.*, **15**, 924 (1914).

² HOROVITZ and PANETH: *Z. physik. Chem.*, **89**, 513 (1915).

ions will be relatively strongly adsorbed whose compounds, with the oppositely charged ions of the ion lattice, are slightly soluble. This conclusion is known as Paneth's adsorption rule. In accord with this rule, Fajans and Beckerath¹ found that thorium *B* (an isotope of lead) and lead ions were quite strongly adsorbed by silver halide sols stabilized by preferential adsorption of halide ions and it is known that the halides of thorium *B* and lead are not easily soluble. Moreover, the adsorption of thorium *B* is greater than that of lead and the halides of the former are less soluble than the latter. Fajans and Beckerath showed further that thorium *B* and lead are not adsorbed by a halide sol stabilized by preferential adsorption of silver ions. This is because the adsorption of the ions in question was not sufficiently great, at the concentration used, to displace the more strongly adsorbed silver ions. Fajans and Frankenburger² found that every fourth to tenth atom of silver in a silver bromide lattice has adsorbed a silver ion from a silver nitrate solution as dilute as 1.5×10^{-5} mols per liter. In spite of this strong adsorption, it is probable that the relative concentrations of lead and silver ions could be so arranged that some lead ions would be adsorbed in the presence of silver.

Beekley and Taylor³ have investigated the relation between the solubility of various silver salts and their adsorbability by silver iodide. The effect of valence was eliminated by choosing salts with univalent anions only. The results of their observations are represented in Fig. 23. The number in parenthesis following the formula of the salt is the relative solubility, silver bromate, the most insoluble salt, being taken as unity. It will be seen that there is nothing approaching a quantitative relationship between solubility and adsorbability. The most that can be said is that the less soluble salts tend to be more strongly adsorbed and the most soluble salts less strongly adsorbed. Thus, among the more soluble ones, silver nitrate is adsorbed more strongly than silver chloride although the former is nine-

¹ *Z. physik. Chem.*, **97**, 478 (1921); cf., also, HAHN, ERBACHER, and FEICHTINGER: *Naturwissenschaften*, **41**, 1196 (1926); *Ber.*, **59 B**, 2014 (1926).

² *Z. physik. Chem.*, **105**, 255 (1923).

³ *J. Phys. Chem.*, **29**, 942 (1925).

teen times as soluble as the latter; and among the less soluble ones, silver acetate is adsorbed much more strongly than silver bromate although the former is eight times as soluble as the latter. Moreover, the jump between the relatively soluble and the relatively insoluble salts is not marked. Thus, the difference in adsorption between bromate and acetate is no greater than

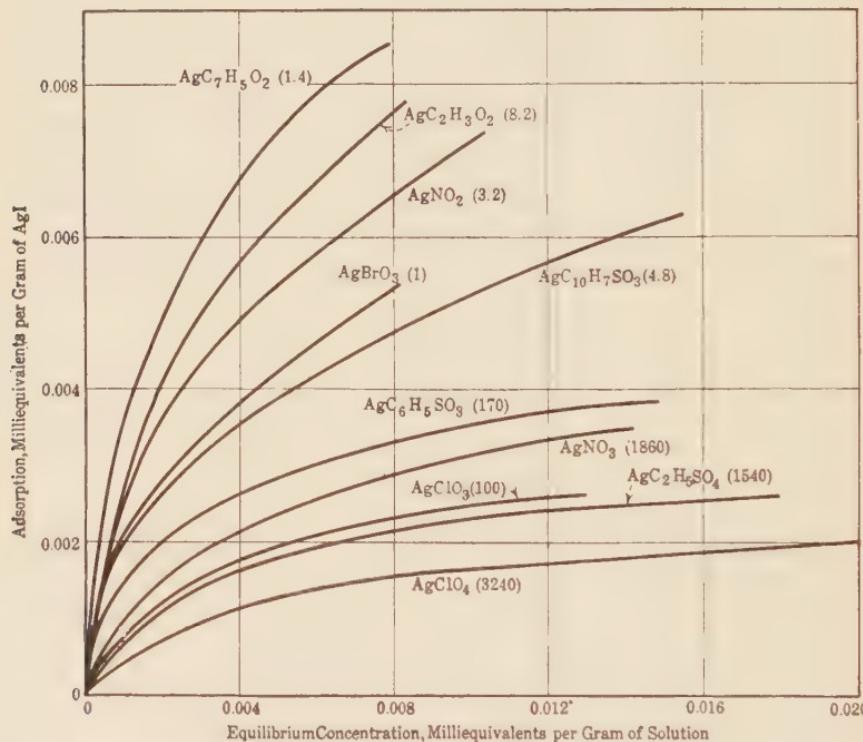


FIG. 23.—Adsorption of silver salts by silver iodide. (Number in parenthesis is relative solubility of silver salts.)

the difference in adsorption between bromate and nitrate, although the ratio of solubilities of the first pair is 8.2 and of the second pair is 100.

The order of adsorption of cations by silver iodide was found by Mukherjee and Kundu¹ to be $\text{Ag} > \text{Al} > \text{Ba}, \text{Ca} > \text{K}$. With the exception of the common Ag^+ ion, the ion with the highest valence is most strongly adsorbed.

¹ Quart. J. Indian Chem. Soc., 3, 335 (1926).

From these observations and others reported in an earlier chapter,¹ it is obvious that solubility is not the only factor which influences the degree of adsorption and may not be the most important factor in certain cases. As already noted,² Fajans considers adsorption of ions by a crystal to take place through the agency of the residual valences of the ions on the surface of the lattice. Thus, if iodide ion is adsorbed by silver iodide, it becomes attached to the silver ion and so becomes an integral part of the silver iodide lattice. In so doing, the adsorbed ion loses its hydration shell,³ the dehydration being accompanied by a marked energy change. From this point of view, it would follow that the greater the affinity of an ion for water, in other words the more highly hydrated it is, the less strongly it will be adsorbed.⁴ It is possible that the order of adsorption of anions by silver iodide would be more nearly the reverse of the order of solubilities if the degree of hydration of the several ions were taken into account. It is probable, however, that there are specific factors other than solubility and degree of hydration which influence the amount of adsorption. While the attempts to evaluate the several factors which account for the specificity of adsorption are highly commendable, it must be clearly recognized that a great deal of work must be done before a quantitative formulation can be made of the several factors which enter into the adsorption process.

The adsorption isotherm for cupric ions by silver bromide was determined by Luther,⁵ who was investigating the mechanism of the photographic desensitizing action of copper salts. The copper salt was added to a suspension of the silver halide and the adsorption measured by a catalytic method based on the catalytic action of cupric ions on the reaction between persulfate and thiosulfate in the presence of iodide ions. The adsorptive power of the coagulated compound was less than that of the suspended salt, indicating that coagulation was accompanied by a growth in primary particles.⁶ The maximum adsorption of the coagulated

¹ P. 187.

² P. 129.

³ FAJANS: *Naturwissenschaften*, **37**, 1 (1921).

⁴ See p. 254 for a detailed discussion of this theory.

⁵ *Trans. Faraday Soc.*, **19**, 394 (1923).

⁶ Cf. p. 214.

salt was found to be approximately 1 mol of Cu⁺⁺ to 400 mols of AgBr.

The silver halides adsorb dyes both from true and colloidal solutions and also adsorb organic colloids such as casein, tannin, gums, and gelatin.¹ The adsorbing power for dyes is in the usual order AgI > AgBr > AgCl.² Sheppard³ found that 1 molecule of the photographic sensitizing dye orthochrome-T-bromide is adsorbed for about two ions of the lattice surface of AgBr at a pH value of 5.5. Frumkin and Obrutschewa⁴ showed that silver iodide exhibits a maximum adsorption for caprylic alcohol at a silver ion concentration of a definite strength. This concentration corresponds to a potential of 0.16 volt as measured with a silver electrode against a normal calomel electrode.

Carey Lea⁵ claimed that freshly precipitated silver iodide adsorbs iodine from an alcohol-water solution of the element; but Germann and Traxler⁶ found that such is not the case. A thoroughly purified sample of the salt does not decolorize a dilute iodine solution. This results only when the sample is not washed so as to remove adsorbed silver nitrate which will react with iodine.

The colloidal silver halides are of particular importance in photography. This subject will be treated in the next chapter.

THE COLLOIDAL HALIDES OF LEAD

With the exception of the fluoride, the halides of lead are much more soluble than the corresponding halides of silver and so are less readily obtained in the colloidal state. The solubilities of the salts in grams per liter are: PbCl₂, 10.8; PbBr, 9.7; and PbI, 0.764. From the von Weimarn theory,⁷ one would not expect any of these salts to be thrown down in the colloidal state from aqueous solutions. Actually, the most soluble lead halide, the chloride, precipitates as a slimy mass which runs through a fine-pored filter paper, when a molar solution of sugar of lead is

¹ REINDERS: *Z. physik. Chem.*, **77**, 677 (1911).

² LÜPPO-CRAMER: *Kolloid-Z.*, **28**, 90 (1921).

³ *Nature*, **118**, 913 (1926).

⁴ *Biochem. Z.*, **182**, 220 (1927).

⁵ *Am. J. Sci.*, [3] **33**, 492 (1887).

⁶ *J. Am. Chem. Soc.*, **44**, 460 (1922).

⁷ See p. 6.

mixed with a 2-molar solution of sodium chloride.¹ The tendency to separate in the colloidal state is, of course, most marked with the least soluble iodide. Stable sols of lead iodide are formed in the presence of protective colloids which prevent the growth of particles by dissolution of the smaller ones and precipitation on the larger ones. By mixing 10 cubic centimeters each of 0.1 normal solutions of lead acetate and potassium iodide with 80 cubic centimeters of 0.05 per cent gelatin, an orange-yellow sol with a beautiful silky luster results. The particles consist of hexagonal plates which exhibit a distinct double refraction when examined with crossed nicols. With 0.3 per cent gelatin, the sol forms more slowly and the particles are much finer but are still crystalline.² After some weeks, the gradual growth of the particles results in precipitation of the sol. This sedimentation can be prevented almost entirely by using sodium protalbinate, so-called, as a protective colloid.³ Five cubic centimeters of a 5 per cent solution of this protector is heated with 15 grams of a 20 per cent solution of lead acetate. The resulting lead "salt" is dissolved in sodium hydroxide and treated with potassium iodide, giving a sol which is reddish brown in transmitted light and greenish yellow in reflected light. After purification by dialysis the sol may be evaporated to dryness without destroying the sol-forming property of the residue.

Large beautifully formed crystals of lead iodide are obtained by allowing a potassium iodide solution to diffuse slowly into a silica gel containing lead acetate.⁴

THE COLLOIDAL HALIDES OF MERCURY

The precipitate formed on adding a solution of an alkali halide to a mercurous salt is a fine crystalline powder. Stable hydrosols of the salt have not been obtained except in the presence of protective colloids. On mixing 0.05 molar solutions of sodium

¹ VAN DER VELDE: *Chem. Ztg.*, **17**, 1908 (1893).

² REINDERS: *Kolloid-Z.*, **21**, 164 (1917); cf., also, LACHS: *J. phys. radium*, **3**, 125 (1922).

³ LEUZE: "Zur Kenntnis kolloidaler Metalle und ihrer Verbindungen," Erlangen, 32 (1904).

⁴ HOLMES: *J. Phys. Chem.*, **21**, 718 (1917); *J. Franklin Inst.*, **184**, 758 (1917).

chloride and slightly acidified mercurous nitrate, strongly double refracting needle-crystals of mercurous chloride 10μ in length are formed. In the presence of 0.3 per cent gelatin, the growth of the crystals is inhibited to such an extent that a stable sol results which is milky bluish white in reflected light and exhibits distinct double refraction when examined with crossed nicols.¹

If a dilute solution of a mercurous salt is treated with a stannous salt, a sol is formed consisting of hydrous stannic oxide with adsorbed mercury. Such a sol is converted into a mercurous halide sol stabilized by stannic oxide by treating with the amount of halogen corresponding to the reaction $2\text{Hg} + \text{X}_2 \rightarrow 2\text{HgX}$ or with the amount of mercuric salt corresponding to the reaction $\text{Hg} + \text{HgX}_2 \rightarrow 2\text{HgX}$.² Very stable mercurous halide sols are prepared for therapeutic use by the interaction of a mercurous salt and alkali halide in the presence of albuminous bodies, followed by dialysis.³ By careful evaporation of the sol or by coagulation with alcohol, a gel results which is peptized by water, alcohol, ether, or benzene. The gel thrown down by an acid is repeptized by thorough washing with water containing a little alkali.

Mercuric chloride and bromide are too soluble to form hydrosols but an iodide sol should result in the presence of a protective colloid. Charitschkow⁴ made colloidal mercuric chloride by the action of hydrogen chloride on a solution of mercuric naphthenate in benzene, toluene, or light petroleum.

¹ REINDERS: *Kolloid-Z.*, **21**, 165 (1917).

² LOTTERMOSER: *J. prakt. Chem.*, [2] **57**, 485 (1898).

³ GALEROSKY: *Pharm. Ztg.*, 230 (1904); *Chemische Fabrik*, Hayden: German Patent, 165282 (1903); *Chem. Zentr.*, II, 1757 (1905).

⁴ *J. Russ. Phys. Chem. Soc.*, **52**, 91 (1920); *J. Chem. Soc.*, **122**, [2] 827 (1922).

CHAPTER XIV

THE SILVER HALIDES IN PHOTOGRAPHY

PHOTOCHEMICAL DECOMPOSITION OF SILVER HALIDES

The sensitiveness of silver chloride to light was probably discovered by Schulze in 1727. Scheele¹ likewise observed the phenomenon and was the first to show that chlorine is liberated in the process and that violet rays are more effective than red or green rays in producing darkening. The darkening is due to the liberation of finely divided metallic silver which colors the salt violet to brown to black. The decomposition with the accompanying darkening is superficial, so that the loss in weight, due to vaporization of the halogen liberated with the silver, is slight when the halide is insolated in mass.² By the aid of the microbalance, Hartung³ showed that thin films of the halides are almost completely decomposed into silver and the halogen on prolonged exposure to sunlight. Thus it was found that more than 96 per cent of the bromine is expelled by insolating thin films of silver bromide in vacuum in the presence of a suitable halogen absorbent. Similarly, 95 per cent of the iodine is expelled from silver iodide and 91 per cent of the chlorine from silver chloride when the containing vessel is filled with air before evacuation, while in the presence of nitrogen the percentage chlorine expelled is 90 per cent and in the presence of hydrogen 95 per cent. Hartung showed conclusively that the decomposition products are always silver and the halogen;⁴ oxygen is not necessary for the action and there is no indication of the formation of a sub-halide in any case.

¹ Cf. MELLOR: "Comprehensive Treatise on Inorganic and Theoretical Chemistry," **3**, 391 (1923).

² Cf. BAKER: *J. Chem. Soc.*, **61**, 728 (1892); RICHARDSON: *Ibid.*, **59**, 536 (1891); KOCH and SCHRADER: *Z. Physik*, **6**, 127 (1921).

³ *J. Chem. Soc.*, **121**, 688 (1922).

⁴ Cf., also, KOCH and KREISS: *Z. Physik*, **32**, 384 (1925); EHLERS and KOCH: *Ibid.*, **3**, 169 (1920).

In this connection, attention should be called to the existence of an optimum concentration at which chlorine attacks silver most readily, the rate of chlorination decreasing rapidly as the concentration of halogen in the surrounding air increases. This recalls the behavior of phosphorus which is not attacked by pure oxygen at room temperature, probably owing to the formation of a thin protective film of oxide.¹

The photographic sensitivity of the silver halides, that is, the sensitivity for latent image formation followed by development, is in the order: bromide > chloride > iodide. In general, the halide is more light sensitive when formed in the presence of excess silver ion in the sense that photochemical decomposition of the so-called silver body can be accomplished by light of longer wave length than must be used to decompose a neutral halide or one formed in the presence of excess alkali halide.² The mechanism of the optical sensitization of silver halide by adsorbed silver ion has been given in an earlier chapter dealing with the photochemical decomposition of zinc sulfide.³ This latter salt is also sensitive to light of longer wave length when formed in the presence of excess zinc ion than when formed in the presence of excess sulfide ion.

Schwarz and his collaborators⁴ claim that the silver halide precipitated with excess halide ion is decomposed by panchromatic light more readily than that formed in the presence of excess silver ion. Since this observation apparently contradicts the experience of the photographer, Schwarz concludes that there must be a fundamental difference between what is known as photographic sensitivity and photo-chemical instability. Thus, the order of light sensitivity of the halides is AgBr > AgCl > AgI, whereas the order of instability determined by the degree of darkening caused by a given exposure to light is AgCl > AgBr > AgI.

¹ Cf. WEISER and GARRISON: *J. Phys. Chem.*, **25**, 61, 349, 473 (1921).

² FAJANS: *Z. Elektrochem.*, **28**, 499 (1922); FAJANS and FRANKENBURGER: *Z. physik. Chem.*, **105**, 255, 273 (1923); FAJANS and STEINER: *Ibid.*, **125**, 275, 307 (1927).

³ See p. 129.

⁴ SCHWARZ and STOCK: *Ber.*, **54**, 2111 (1921); *Z. anorg. Chem.*, **129**, 41 (1923).

While the observations of Schwarz may be accurate, one cannot be sure that he compared his silver and halide bodies under identical conditions. Thus he finds his halide body to be more sensitive to white light than the silver body but he does not tell us whether the size and physical character of the particles formed in the presence of excess silver nitrate are the same as the particles formed in the presence of excess alkali halide. Since the solvent action of the alkali halide tends to produce larger crystals, it is probable that the crystals of the halide body were larger than those of the silver body. If so, this might account for a part, at least, of the greater instability of the halide body, since it has been demonstrated conclusively that the larger particles of a given halide emulsion are the more light sensitive. Moreover, Schwarz determined the extent of decomposition in a given case from the amount of halogen evolved. Since silver nitrate will react with the halogens, the amount of halogen liberated by the action of light on the silver body may not be and probably is not a true measure of the magnitude of the primary light process.

In a private letter to the author, Sheppard says:

Only in the case of the photographic sensitivity, that is, the sensitivity for latent image formation followed by development, can we definitely say that the silver halides rank in the order: bromide > chloride > iodide. In the case of visible image formation, comparison has not been definitely made on the basis of equal state of dispersity and adsorption, in which case we might find the iodide more sensitive than the bromide. Finally, if we come down to absolute photo-chemical sensitivity in terms of amount of energy necessary to give a definite amount of photo-product, then if we accept Eggert and Noddack's results on the applicability of Einstein's photo-chemical equivalence law to the silver halides, we must say that they have the same fundamental quantum sensitivity, unless we express the sensitivity in terms of limiting wave length or limiting quantum which can give silver atoms. Since the experimental determination of this limiting wave length is very difficult and the results very questionable at present, I do not think we can speak very decisively on that point. Theoretically, if we regard the limiting quantum as determined by the heat of formation, we should expect the sensitivity in this sense to be in the order: $\text{AgI} > \text{AgBr} > \text{AgCl}$, these being in reverse orders of their heats of formation, and, again, the lattice energies, as a whole, are in the same order, although the differences of the lattice energies are less than for the heats of formation.

Just as in the case of zinc sulfide, a small amount of moisture is essential for the photo-chemical decomposition of the silver halides.

SOLS OF SILVER IN SILVER HALIDES

The Photo-halides.—The colored products formed by the action of light on the silver halides have been termed photo-halides by M. Carey Lea.¹ This investigator pointed out that the varicolored substances having a slight excess of silver over that required by the formula AgX could be prepared by incomplete chemical reduction of the silver halides and subsequent extraction with silver solvents. Thus, silver chloride can be prepared in the following gradations of color: white, pale flesh, pale pink, rose, copper, red purple, dark chocolate, and black. Lea regarded the photo-halides as lakes or adsorption compounds of normal silver halide and silver sub-halide, the color depending on the method of formation. Lea claimed to have prepared also a "soluble" allotropic form of silver of various colors and suggested that the color of the photo-halides might be due to the "soluble" silver. Lüppo-Cramer showed conclusively, however, that Lea's "allotropic" silver was colloidal silver. By mixing sols of silver halides with silver sols, coagulating the mixture, and then extracting with nitric acid, red, blue, or violet, photo-halides were obtained identical in appearance with Lea's preparations and containing a slight excess of silver above that necessary for the normal salt. That the photo-halides consist of silver dispersed in silver halide was further demonstrated by Lorenz and Eitel who exposed optically clear silver halides to light in the ultramicroscope. Under these conditions, the crystals, clear at first, began to darken and at the same time to show ultramicroscopic particles of silver which grew rapidly. The metallic clouds produced in crystals by light were found to be quite similar to those formed during the electrolysis of the fused salts.²

Crystallized photo-halides were prepared by Reinders³ by allowing the silver salt to crystallize from an ammoniacal solution

¹ *Am. J. Sci.*, [3] **33**, 349 (1887).

² LORENZ and EITEL: *Z. anorg. Chem.*, **91**, 57; LORENZ and HIEGE: *Ibid.*, **92**, 27 (1915).

³ *Kolloid-Z.*, **9**, 10 (1911).

containing colloidal silver. In the presence of gelatin, the latter was taken up by the crystallizing halide (but not by the colloidal silver) yielding a product which was more light sensitive than the pure salt.

The Latent Image.—In photography with development, the exposures of the sensitive plate to light are insufficient to cause any microscopically visible change in the silver halide. Yet some change does take place since the application of suitable reducing agents causes the so-called "latent image" to develop. The nature of the latent image has been a subject of controversy for a long time. Owing to the very slight change in silver halide on short exposure, it has been quite commonly assumed that the latent image is a physical or allotropic modification of silver halide. Namias¹ assumed polymerization; Hurter and Driffield² depolymerization; Bredig,³ mechanical disintegration; Jones,⁴ a labile form; and Bose,⁵ mechanical strain. Bancroft⁶ points out that all these assumptions, and the further one of von Tugolessow⁷ that the latent image is an oxidation product, are untenable since all the phenomena of the latent image can be duplicated by immersing the plate in a solution of a weak reducing agent, such as sodium arsenite.⁸ It appears, therefore, that the latent image is some reduction product of silver bromide. It has been commonly assumed to be either a sub-halide⁹ or a series of sub-halides of varying composition.¹⁰ These assumptions appear unfounded since no one has been able to prepare any sub-halide derived from the chloride, bromide, or iodide of silver and it is improbable that any exists.¹¹

¹ *Chimie photographique*, 102, 110 (1910).

² *Phot. J.*, **22**, 149 (1898).

³ Eder's *Jahrbuch der Photographie*, **13**, 365 (1899).

⁴ "Science and Practice of Photography," **1**, 383 (1904).

⁵ *Phot. J.*, **26**, 146 (1902).

⁶ *Trans. Faraday Soc.*, **19**, 243 (1923).

⁷ *Phot. Correspondenz*, **40**, 594 (1903).

⁸ BANCROFT: *J. Phys. Chem.*, **14**, 294 (1910); PERLEY: *Ibid.*, **14**, 689 (1910); CLARK: *British J. Photography*, **69**, 462 (1922).

⁹ LUTHER: *Z. physik. Chem.*, **30**, 680 (1899).

¹⁰ TRIVELLI: *Chem. Weekblad*, **7**, 321, 350, 381, 404 (1910); **8**, 101 (1911); **9**, 232, 248 (1912).

¹¹ BAUR: *Z. physik. Chem.*, **45**, 613 (1903); REINDERS: *Ibid.*, **77**, 213, 356, 677 (1911).

A second assumption is, that the latent image consists of an infinitesimally small quantity of metallic silver which acts as a germ or nucleus¹ facilitating the reduction of the surrounding silver halide. This view has been criticized on the grounds that the latent image shows none of the reactions of metallic silver;² does not exhibit the potential of colloidal silver,³ and does not account for the facts of development and solarization (image reversal).⁴ To get around these difficulties, the latent image was assumed to consist of a phase of variable composition with silver chloride the end term, that is, a solid solution probably of silver in silver halide.⁵ It is much more probable that the latent image is an early stage of photo-halide formation and is, therefore, a colloidal solution of metallic silver dispersed in silver halide⁶ and adsorbed thereby.⁷ This view seems to account best for all the reactions of the latent image including the effect of oxidizing agents and the acceleration in reduction shown in developability. Thus, the latent image is destroyed so far as chemical development is concerned, by treating with chromic acid (2 per cent $\text{CrO}_3 + 1$ per cent H_2SO_4). On the other hand, if the plate is considerably over-exposed, and the silver halide subsequently removed by sodium thiosulfate, it is possible to develop an image by an acid silver developer such as silver nitrate plus ferrous sulfate and acetic acid. Lüppo-Cramer⁸ attributes this behavior to the formation of colloidal silver inside the grain by prolonged exposure. Under ordinary conditions, these exposed particles are protected by silver halide and so cannot initiate reduction with a developer after the surface latent image is removed by an

¹ W. OSTWALD: "Lehrbuch allgemeinen Chemie," 2nd ed., **2**, 1078 (1893); ABEGG: *Archiv. wiss. Phot.*, **1**, 268 (1899); LORENZ: *Z. Elektrochem.*, **7**, 277 (1900).

² LÜPPO-CRAMER: *Phot. Correspondenz*, **38**, 145 (1901).

³ SHEPPARD and MEES: *Proc. Roy. Soc. (London)* **76 A**, 217 (1905); **78 A**, 461 (1907); LÜPPO-CRAMER: *Kolloid-Z.*, **2**, 103, 135 (1908).

⁴ BANCROFT: *J. Phys. Chem.*, **17**, 93 (1913).

⁵ LÜPPO-CRAMER: *Der latente Bild* (1911); REINDERS: *Z. physik. Chem.*, **77**, 213 (1911).

⁶ ABEGG and LORENZ: *Loc. cit.*

⁷ BANCROFT: *J. Phys. Chem.*, **17**, 93 (1913); *Trans. Faraday Soc.*, **19**, 243 (1923).

⁸ "Photo. Probleme" (1907).

oxidizing agent. On the other hand, if the protecting silver halide is first removed, the nuclei are uncovered and can act as centers for the deposition of silver from a supersaturated solution. Lüppo-Cramer prepared synthetic photo-halides that behave in the same way as the latent image. If the excess silver is not removed from the former by the use of too strong an oxidizing agent, they are readily developable; but treatment with chromic acid destroys this property. It thus appears that the latent image does show certain of the reactions of metallic silver. There is, of course, no reason why colloidal silver protected by silver halide should show the same electrical potential as silver in mass.

One objection to considering the latent image as a photo-halide is that the latter is highly colored, whereas the former never is, under ordinary conditions. The difference is apparently merely a question of the amount and degree of dispersity of the colloidal silver. Thus if plates are exposed to the action of x-rays before exposure to ordinary light, the x-ray image develops as a pinkish coloration in contrast with the gray-green tone of the untreated halide.¹ Lüppo-Cramer² attributes this difference to the higher degree of dispersity of the silver in the grains exposed to x-rays. The effect of the latter is to produce a much larger number of nuclei per grain and hence a larger number of smaller particles with the resulting pink tone. This is in line with the observation that the color of silver hydrosols passes from yellow through brown, red, purple, and blue to gray with increasing particle size.

Further reference to the nature of the latent image will be made in the section on Photographic Sensitivity.

PHOTOGRAPHIC EMULSIONS

The photographic emulsions, so-called, are suspensions of the light-sensitive silver halides in a colloidal medium such as collodion or gelatin. Layers of silver bromide prepared by sedimentation of the sols have been used for photographic investi-

¹ LÜPPO-CRAMER: "Die Rontgenographie," 29, (1909).

² *Phot. Correspondenz*, 47, 337, 527 (1910).

gations¹ and for plates sensitive to the ultraviolet;² but for most purposes, the sols formed in the presence of gelatin are employed. Since the properties of silver halide sols vary considerably depending on whether they are formed in the presence of a slight excess of soluble silver salt or in the presence of a slight excess of alkali halide, it has been found practicable to distinguish two classes of silver halide emulsions.

Technical emulsions formed in the presence of excess soluble silver salt, usually silver nitrate, include "wet collodion" which is used extensively in photo-mechanical work and collodion emulsions for printing out. Silver ions adsorbed on the halide ions of the silver halide lattice sensitize the primary photochemical decomposition of the salt, as already noted. The silver nitrate may also act as a chemical sensitizer by reacting with bromine liberated by the primary light process.

The group of emulsions formed in the presence of excess alkali halide comprise both positive and negative emulsions for development. The excess soluble halide influences the physical character of the precipitated salt chiefly by acting as a solvent in the "ripening" process which will be considered in a later paragraph. In the preparation of most negative emulsions, soluble iodide up to 5 per cent of the silver halide is added to the alkali bromide so that the resulting silver bromide contains a small amount of silver iodide. Emulsions used for photographic papers may consist of nearly pure silver bromide, of mixtures of silver bromide and chloride, or, in some cases, of pure silver chloride.

The precipitation of the silver halide must be carried out under carefully controlled conditions in order to prevent flocculation of the particles and to ensure uniform dispersion throughout the gelatin. The action of gelatin as a protective colloid tends to give a fine-grained uniform precipitate which consists in all cases of crystalline particles. In commercial positive emulsions, the particles seldom exceed 0.3μ in diameter and, in negative emulsions, 3 to 4μ . Actually, there is usually a wide variation in grain size. Sheppard and his coworkers³ have determined the

¹ HERSCHELL: *Cf. HUNT, "Researches on Light," London, 66 (1859); SCHAUM: Eder's *Jahrber. Phot.*, 74 (1904); WEISZ: *Z. physik. Chem.*, **54**, 322 (1906).*

² SCHUMANN: *Sitzb. Akad. Wiss. Wien, Abt. IIa*, **102**, 994 (1893).

³ WIGHTMAN, SHEPPARD, and TRIVELLI: *J. Phys. Chem.*, **27**, 1, 141 (1923).

proportion of grains of different size in given emulsions and have thereby established the grain-size frequency, that is, the relative proportion of grains of different sizes in, say, 1000 grains. The statistical curves of most emulsions can be expressed by probability formulas of the exponential or (modified) Gaussian type. The distribution is of particular importance because of the relation between grain size and sensitivity in a given emulsion.

PHOTOGRAPHIC SENSITIVITY

Mention has been made of the observations of Fajans on the optical sensitizing of silver halides by adsorbed silver ion. The observed effects involve the shifting of the quantum limit, hv , capable of reducing a silver ion to metallic silver. Photographic sensitivity or developable sensitivity (latent image) of silver halide grains is a different effect which will be given special consideration.

Sheppard¹ defines the sensitivity of a photographic emulsion by the exposure in candle-meter-seconds (product of intensity of light times time of exposure) necessary to give a certain normal negative with chemical development behind a sensitometer table. Practically, silver bromide emulsions may be prepared which range from the Lippmann type (speed 1) to the high-speed type (speed 150,000). A number of conditions are operative in determining the sensitivity:

Ripening.—The speed of an emulsion of the Lippmann type may be increased by ripening in the sense of digestion of the emulsion at temperatures up to 80° in the presence of silver bromide solvents such as ammonia or soluble bromide. Since the ripening process consists chiefly in the dissolution and reprecipitation of silver bromide² with the consequent coarsening of grain, it has been generally assumed that a coarse grain is more sensitive than a fine one. This is only partly true since grains of the same size may differ in sensitivity when present in different emulsions. Thus, mere ripening of an emulsion of the Lippmann type might increase the speed five hundredfold or more, but it

¹ Colloid Symposium Monograph, **1**, 346 (1923).

² SHEPPARD: Colloid Symposium Monograph, **1**, 346 (1923); SHEPPARD and LAMBERT: *Ibid.*, **4**, 281 (1926); cf., however, RENWICK: *Phot. J.*, **48**, 324 (1924).

will not give an emulsion of the high-speed type. The latter are, in general, prepared with relatively high concentrations of the reacting silver salt and alkali bromide, low gelatin concentration, high temperature of mixing, and retarded addition, so that the dispersity of grain is determined at mixing and is altered but little by ripening.¹ The extended investigations of Sheppard and his collaborators on the grain-size distribution in a large number of different emulsions disclose that while coarseness of grain is a necessary condition of high speed it is not a sufficient condition.² In general, the sensitivity increases statistically with the size of grain in one and the same emulsion, but with different emulsions there is no necessary relation between average grain size and sensitivity. The absence of a definite correlation between grain size and sensitivity suggests that some other factor is operating.

The "Sensitivity Substance."—It is a well-known fact that a much faster plate is obtainable with gelatin than with dry collodion. The formal way to account for this is to assume that gelatin is a better sensitizer than collodion since gelatin will react with bromine more readily than collodion does and hence is a better depolarizer. This cannot be the whole explanation since different gelatins show marked differences in their sensitizing action. For the same reason, it is not permissible to attribute the superiority of gelatin over collodion to the possibility of producing larger individual crystals of silver bromide in the former medium than in the latter.

Almost a score of years ago Lüppo-Cramer³ showed that the sensitivity of ripened photographic plates was diminished appreciably by treatment with chromic acid before exposure, followed by thorough washing. Lüppo-Cramer accounted for this behavior by postulating the existence of "Reifungskeime" or sensitive nuclei of highly dispersed colloidal silver.⁴ Sheppard⁵ and his collaborators showed that practically every kind of photographic emulsion could be desensitized in this way and

¹ TRIVELLI and SHEPPARD: "The Silver Bromide Grain of Photographic Emulsions," Van Nostrand, 104 (1921).

² SHEPPARD: Colloid Symposium Monograph, **1**, 346 (1923).

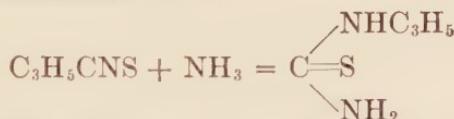
³ *Phot. Mitteilung*, 328 (1909).

⁴ Cf., also, RENWICK: *J. Soc. Chem. Ind.*, **39**, 156 T (1920).

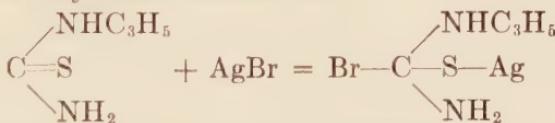
⁵ SHEPPARD, WIGHTMAN, and TRIVELLI: *J. Franklin Inst.*, **196**, 779, 802 (1923).

pointed out the relation between this phenomenon and the destruction of the latent image by chromic acid and other oxidizing agents. It was shown further in the Eastman Kodak Company's laboratories, that the smaller grains were reduced relatively more in sensitivity than the larger ones by the chromic acid treatment.¹ It was evident, therefore, that the silver halide grain contains a sensitivity substance other than silver bromide which increases photographic sensitivity and is destroyed by chromic acid.

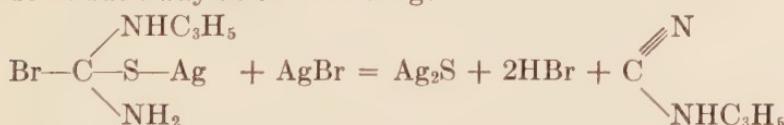
A fundamental advance which made possible the isolation and identification of the sensitivity substance was made at the Eastman Kodak Company by R. F. Punnett. He succeeded in obtaining from a gelatin which yielded highly sensitive emulsions an extract which could be added to emulsions of low sensitivity and thereby increase both their speed and density-giving power. A systematic search for this sensitizing material was made by Sheppard² who found it to consist for the most part of certain organic sulfur-containing substances, such as mustard oil and bodies derived therefrom. The action of these may be illustrated by taking allyl mustard oil as an example. This compound reacts with ammonia as follows:



the thioearbamide formed reacting with silver halide in excess to give a relatively insoluble silver salt



These compounds do not appear to be the actual sensitizers, for on treating with slightly alkaline solutions, silver sulfide is formed in some such way as the following:



¹ Cf., also, CLARK: *Phot. J.*, **63**, 230 (1923).

² Colloid Symposium Monograph, **3**, 76 (1925).

Since definite sensitization is obtained only after treatment of the emulsion at sufficiently high pH value to produce Ag_2S , it is probable that this compound is the effective sensitizer.

The existence in gelatin of varying amounts of sulfur bodies which yield the sensitizer, silver sulfide, accounts for the facts that gelatin emulsions are more sensitive than collodion emulsions and that gelatin emulsions made with different samples of gelatin but otherwise similar, may exhibit marked differences in sensitivity. The action of chromic acid in cutting down the sensitivity substance is due sometimes, perhaps, to destruction of the mustard oil impurity, but more generally to distortion of silver sulfide nuclei.

Mechanism of the Sensitization.—Trivelli and Sheppard¹ first showed that the photochemical decomposition of the octahedral surfaces of silver bromide crystals does not take place simultaneously over the entire surface of the crystal but starts in isolated points. Similarly, Hodgson² found that if the development of exposed single grains was carried out with a dilute developer and interrupted at an early stage before the grain was completely reduced, the development was observed to commence at one or more isolated points on the grain. Svedberg³ and Toy⁴ showed these sensitivity centers to be statistically distributed among the grains in a purely haphazard manner. Further, it appeared to be sufficient for a grain to have one such development center in order to be completely developable while the chance of a grain having one such center at a given exposure to light increased with the size of the grains in one and the same emulsion. As already noted, Sheppard, Wightman, and Trivelli⁵ showed that treatment of an emulsion with chromic acid prior to exposure desensitizes the smaller grains to a greater extent than the larger ones. The sensitivity spots therefore must exist prior to exposure and are not produced either by exposure⁶ or by

¹ "The Silver Bromide Grain of Photographic Emulsions," 83 (1921); *Phot. J.*, **63**, 334 (1923); cf., also, LORENZ and EITEL: *Z. anorg. Chem.*, **91**, 57 (1915).

² *J. Franklin Inst.*, **184**, 705 (1917).

³ *Phot. J.*, **62**, 180, 310 (1922).

⁴ *Phil. Mag.*, [6] **44**, 352 (1922); *Trans. Faraday Soc.*, **19**, 290 (1923).

⁵ *J. Franklin Inst.*, **195**, 674 (1923).

⁶ Cf., however, SILBERSTEIN: *Phil. Mag.*, [6] **44**, 257, 956 (1922).

development. It now appears that these nuclei are silver sulfide particles which exist at certain points in the crystal lattice of the bromide, causing a localized concentration of the photo-chemical effect whereby the same light energy which would have produced silver atoms dispersed about the silver halide crystal, produces the same number immediately contiguous to the silver sulfide, thereby affording a nucleus for development for a correspondingly smaller exposure.

The latent image therefore consists essentially of colloidal silver on nuclei of silver sulfide. Desensitizing by chromic acid is due primarily to the destruction of these silver sulfide nuclei which are active in initiating the localized decomposition. Any residual sensitivity after the chromic acid treatment is probably due to nuclei which are protected by the silver halide. This theory does not exclude the action of colloidal silver in promoting sensitivity but Sheppard¹ believes that this effect is of secondary importance.

Action of Silver Iodide.—It has been pointed out that silver iodide up to 5 per cent is usually present in silver bromide emulsions. More than 5 per cent is detrimental since it reduces the developability. Now the crystal structure of silver bromide is simple cubic of open type, while that of silver iodide is tetrahedral of a much more compact form; x-ray analysis² shows that the presence of silver iodide in the silver bromide lattice enlarges the lattice and consequently induces changes in the interatomic forces. This produces a condition of strain which renders the mixture more light sensitive than the simple bromide lattice. The effect is, perhaps, still further enhanced by the presence of the foreign colloidal particles of silver sulfide within the lattice.

An examination of certain high-speed iodo-bromide emulsions by Renwick and his collaborators³ disclosed the presence of more iodide in the larger grains than in the smaller ones. It has been inferred from this that the apparent relation of size of grain to sensitivity in the same emulsion may be due entirely to the greater proportion of iodide in the larger grains. Sheppard and Trivelli⁴ disproved this assumption by showing that the larger

¹ Colloid Symposium Monograph, **3**, 97 (1925).

² WILSEY: *J. Franklin Inst.*, **200**, 739 (1925).

³ RENWICK and SEASE: Colloid Symposium Monograph, **2**, 37 (1925); *Phot. J.*, **64**, 360 (1924).

⁴ *J. Franklin Inst.*, **203**, 829 (1927).

grains of a silver bromide emulsion free from iodide are markedly more sensitive on the average than the smaller grains.

DEVELOPMENT

The development of the exposed photographic plate consists essentially in the conversion of silver ions to metallic silver. Technically, two types of development are distinguished: (1) "physical" development, so-called, in which the silver which builds up the developed image on the colloidal silver nuclei of the latent image, is obtained from soluble silver salt in the developing solution. Owing to the high concentration of silver ions, the reduction potential is low and reducers are employed in acid solution. (2) "chemical" development in which silver is formed by reduction of the solid silver halide grains themselves, the reduction being catalyzed by the silver nuclei of the latent image. In this case, higher reduction potentials are employed, the solutions being alkaline.

The theory of the development of the latent image commonly held is that the developer is a reducing agent sufficiently powerful to reduce exposed silver bromide which has a nucleus in each grain on which the deposition of silver can take place, but not powerful enough to reduce unexposed silver bromide.¹ Baneroft² points out that this theory is in itself inadequate since measurements of the electromotive force of developers and of silver bromide before and after exposure fail to substantiate the theory. Recently Baneroft³ has formulated the problem and has restated his theory of photographic development in the following way:

1. A photographic developer must be a fairly strong reducing agent, and yet it is apparently impossible to produce a satisfactory negative with stannous chloride,⁴ m-aminophenol, formaldehyde, or gallic acid.⁵

2. There is no appreciable difference between the electromotive forces of unexposed silver bromide and of that which has received a short exposure.

¹ Cf., for example, METZ: *Phot. J.*, **60**, 281 (1920).

² *J. Phys. Chem.*, **17**, 93 (1913).

³ *Trans. Faraday Soc.*, **19**, 243 (1923).

⁴ SEYEWETZ: "Le développement de l'image latente en photographie," **18**, 31 (1899).

⁵ EDER: *Phot. Correspondenz*, **36**, 380 (1899).

3. All developers develop gelatin-free silver bromide readily, even though the silver bromide has not been exposed to light.
4. Most developers give negatives after very short exposures and positives after very long ones.
5. Some developers give positives with very short exposures.
6. With any one developer, the exposure necessary to cause a change from negative to positive varies with varying concentration of the developer.
7. Very dilute developers act like light and decompose silver bromide without developing it.
8. Some developers work rapidly and others slowly; the difference is not always one of reducing power as measured by electromotive force, though this is unquestionably a factor.
9. Bromide is very effective with some developers and less so with others.

The fact that we get a negative with one developer and a positive with another for the same exposure shows that the potentials of exposed and unexposed silver bromide are not the sole factors. If they were, we should always get a negative with one exposure and always a positive with another. The developers must therefore have other functions than those of reducing agents of varying strengths. The simplest assumptions seem to be that we have selective adsorption and thereby markedly varying concentrations at the surfaces of the silver bromide grains. If the reducing agent is adsorbed much more strongly by exposed silver bromide than by unexposed silver bromide, the former will develop more rapidly than the latter and we shall get a negative. If the reducing agent is adsorbed more strongly by the unexposed silver bromide than by the exposed silver bromide, we shall get a positive. If there is not much difference in the adsorptions, we shall have exposed and unexposed silver bromide developing at so nearly the same rate that we get a more or less uniform fogging. By the adsorption theory we are thus able to predict the possible existence of the three types of fairly strong reducing agents that we actually encounter; but that does not necessarily mean that the developers really behave in this way. Until some independent proof is furnished, the theory remains an assumption *ad hoc*.

Sheppard¹ is likewise of the opinion that adsorption of the reducer to the silver halide grain is the first phase of development. He suggests that the free silver ions of the crystal lattice hold ions of the reducer by electro-affinity, the adsorption complex thus formed breaking down in the presence of the nuclei of

¹ SHEPPARD and MEYER: *J. Am. Chem. Soc.*, **42**, 690 (1920).

colloidal silver. Selective adsorption doubtless plays an important role also in the effects of certain dye stuffs, some of which accelerate development and others of which desensitize the halides to such an extent that development can be carried out in strong yellow or even white light.¹

Bancroft believes that the selective adsorption which he postulates involves more or less peptization and that there exists a transition from weakly peptizing, strongly reducing to strongly peptizing, weakly reducing developers, the furthest examples of the latter giving direct solarized or reversed images. In support of his view, Bancroft succeeded in destroying the developability of an exposed plate by washing with elon (metol) containing no alkali, so as to exclude reduction. Sheppard² questions whether this is truly a case of peptization of the latent image and suggests that it may be due to slight etching of the surface layers of the silver halide by the reducers which form soluble complexes with silver halides. In the same connection, Sheppard points out that the production of direct positives by development is associated with the formation of "dichroic fogs," colored forms of colloidal silver produced when a solvent for silver halide is present in the developing solution.

In conclusion, it may be mentioned that the essential difference between the older theories of development and the adsorption theory, as outlined by Bancroft, is that the former treats the problem as one primarily of equilibrium relations whereas the latter regards it as essentially a question of reaction velocities. From either point of view, the influence of diffusion and the effect of the developer on the gelatin must be taken into account.

¹ LÜPPÖ-CRAMER: *Negativentwicklung bei hellem Lichte (Safraninverfahren)*. Ed. Liesegang's Verlag M. Eger, Leipzig (1921).

² Bogue's "Theory and Application of Colloidal Behavior," **2**, 776 (1924).

IV

COLLOIDAL FERROCYANIDES

CHAPTER XV

THE COLLOIDAL FERROCYANIDES

GENERAL PROPERTIES

The interaction of dilute solutions of metallic salts and alkali or alkaline earth ferrocyanides yields gelatinous precipitates of the metallic ferrocyanides. If the solutions are concentrated, the mass sets to a stiff jelly in every case. The gels adsorb ferrocyanide ions strongly, even in the presence of an excess of the metallic ion; hence, the precipitated salt is contaminated more or less by the alkali or alkaline earth ferrocyanide used in its formation. Thus, with potassium ferrocyanide and copper chloride, the formula of the precipitate is represented by Duclaux¹ as $\text{Cu}_m\text{K}_n[\text{Fe}(\text{CN})_6]^{\frac{n}{2}}$ where $m + \frac{n}{2} = 2$. With an excess of copper chloride the value of n lies between 1.3 and 2. Duclaux believes the potassium ferrocyanide to be combined with the copper salt forming a series of definite double salts. It is more likely, however, that the gel is copper ferrocyanide with potassium ferrocyanide adsorbed in varying amounts depending on the relative concentrations of the salts and the conditions of precipitation. This does not preclude the formation of definite double salts under certain conditions; but the composition of the precipitated gel can be varied continuously over such a wide range that the existence of definite double salts is not established simply by the analysis of an amorphous mass.

That it has been the practice to assign formulas to the different gels whenever an analysis was made is evidenced by the large number of types of double salts and molecular compounds of double salts that are assumed to exist.² One is pretty safe in

¹ *J. chim. phys.*, **5**, 29 (1907).

² E.g., see WILLIAMS: "The Chemistry, Manufacture, and Estimation of Cyanogen Compounds," 94 (1915); ROSCOE and SCHORLEMMER: "Treatise on Chemistry."

saying that most of the amorphous masses which have been given a complex formula are not definite compounds but are mixtures or adsorption complexes. The field of the complex and double ferrocyanides should be investigated thoroughly in the light of the phase rule and modern colloid chemistry. Until this is done it is a hopeless task to attempt to separate the "wheat from the tares." It appears, however, that the ferrocyanides of copper, cobalt, cadmium, ferrous and ferric iron, aluminum, lead, manganese, nickel, and zinc can be prepared pure by adding calcium ferrocyanide or hydroferrocyanic acid to an excess of a solution of the metallic salt or by dissolving the carbonates or hydroxides in the dilute acid.¹ The ferrocyanides of copper, zinc, and iron will be considered in detail, the first two in the present chapter and the last in a separate chapter on "Prussian Blue."

COPPER FERROCYANIDE

Colloidal solutions of copper ferrocyanide may be prepared by mixing very dilute solutions of potassium ferrocyanide and copper sulfate.² Gurchot³ dissolved 1 gram each of the two salts in 3000 cubic centimeters of water and mixed the resulting solutions rapidly. The brown sol was quite stable, showing no signs of agglomeration on long standing. More concentrated sols may be obtained by the use of protecting agents⁴ such as gelatin and sugar or by peptization of the freshly formed gel. Graham used oxalic acid or ammonium oxalate as a peptizing agent but there is no point in this as the gel is carried into colloidal solution by thorough washing, preferably by the aid of the centrifuge.⁵ The purity of the sol is increased by subjecting it to dialysis in the cold. The particles of the sol are negatively charged, probably owing to preferential adsorption of ferrocyanide ion. A quantity of sol containing 9.6×10^{-6} gram atoms of potassium required for coagulation the amounts of the several ions given in

¹ WILLIAMS: "The Chemistry, Manufacture, and Estimation of Cyanogen Compounds" (1915).

² GRAHAM: *Phil. Trans.*, [1] **151**, 183 (1861).

³ *J. Phys. Chem.*, **30**, 90 (1926).

⁴ LOBRY DE BRUYN: *Rec. trav. chem.*, **19**, 236 (1900).

⁵ WEISER: *J. Phys. Chem.*, **30**, 1530 (1926).

Table XXXV. Duclaux¹ points out that these precipitation values are approximately equivalent, irrespective of the valence, and are of the same order as the potassium ion concentration,

TABLE XXXV.—PRECIPITATION OF COLLOIDAL $\text{Cu}_2\text{Fe}(\text{CN})_6$ CONTAINING 9.6×10^{-6} GRAM ATOMS OF POTASSIUM

Ion	Valence	Amount required for precipitation, gram equivalent $\times 10^{-6}$
Silver.....	1	6.6
Copper.....	2	3.4
Aluminum.....	3	5.8
Iron.....	3	6.2
Uranyl.....	2	15.0
Barium.....	2	48.0
Magnesium.....	2	98.0
Potassium.....	1	240.0

provided one takes the first four ions and disregards the last four. On the basis of these and similar data on hydrous ferric oxide sol, he considers the precipitation process to be a definite stoicheometric chemical action, a double decomposition of the ordinary type. This conclusion is not in accord with the facts, even if one were permitted to disregard the last four ions. The precipitation concentration expressed in equivalents is different for each ion and has no necessary connection with the potassium ion concentration. In accord with the usual rule, the precipitating power of an electrolyte is determined by the adsorbability of the precipitating ion, which is, in general, greater the higher the valence, and by the adsorbability of the ion having the same charge as the sol. This is illustrated by some observations of Sen² recorded in Table XXXVI. In part A are given the precipitation values of salts with cations of varying valence. It will be seen that the elements divide themselves into three well-defined groups depending on the valence.³ In part B are given the precipitation values of potassium salts arranged in decreasing

¹ *J. chim. phys.*, **5**, 29 (1907).

² *J. Phys. Chem.*, **29**, 517 (1925).

³ Cf. PAPPADÀ: *Gazz. chim. ital.*, **41**, (2) 470 (1911).

TABLE XXXVI.—PRECIPITATION CONCENTRATION OF ELECTROLYTES FOR COLLOIDAL $\text{Cu}_2\text{Fe}(\text{CN})_6$

<i>A</i> Salts with cations of varying valence		<i>B</i> Potassium salts	
Salts	Precipitation concentration, milliequivalents per liter	Salts	Precipitation concentration, milliequivalents per liter
KCl.....	35.6	KNO ₃	28.7
NiCl.....	92.5	KBr.....	27.5
Ba(C ₂ H ₃ O ₂) ₂	0.890	K ₂ SO ₄	47.5
BaCl ₂	0.915	K ₂ HPO ₄	47.5
SrCl ₂	1.075	K ₂ CrO ₄	80.0
MgSO ₄	1.520	K ₂ (C ₄ H ₄ O ₆).....	95.0
Al ₂ (SO ₄) ₃	0.175	K ₂ C ₂ O ₄	170.0
Ce(NO ₃) ₃	0.102	K ₃ Fe(CN) ₆	205.0
Th(NO ₃) ₄	0.150	K ₄ Fe(CN) ₆	260.0

order of precipitating power, which is the order of increasing adsorption of the anions, on the assumption that the most strongly adsorbed anion has the most pronounced stabilizing action.

Frankert and Wilkinson¹ determined the acidity or alkalinity developed on shaking solutions of potassium salts with powdered copper ferrocyanide. The hydrogen ion concentration varies from slightly acid with the weakly adsorbed chloride to highly alkaline with the strongly adsorbed ferrocyanide. The order of adsorption of anions based on the acidity developed is: $\text{Fe}(\text{CN})_6^{4-} > \text{HPO}_4^{2-} > \text{OH}^- > \text{Fe}(\text{CN})_6^{3-} > \text{SO}_4^{2-} > \text{Cl}^- > \text{NO}_3^-$. It will be noted that the order is similar to the one deduced from precipitation data for ions common to both series. It is probable that the series would be more nearly alike for the two sets of experiments if the same sample of copper ferrocyanide were employed.

Some observations by Bhatnagar² may prove to be of importance for the theory of the mechanism of the process of coagulation by electrolytes. Various sols were prepared, including

¹ *J. Phys. Chem.*, **28**, 651 (1924).

² BHATNAGAR, MATHUR, and SHRIVASTAVA: *J. Phys. Chem.*, **28**, 387 (1924).

copper ferrocyanide, and coagulated by electrolytes with precipitating ions of varying valence. By means of a special elutriating device, it was found that for sols of one size of particle, the ratios of the elutriating velocities for the particles of the coagula obtained by salts with monovalent, divalent, and trivalent precipitating ions are 1:2:3. A close relationship is thus indicated between size of particles found by agglomeration and the valence of the precipitation ion. In the case of a spherical particle falling in a viscous liquid, the velocity of fall, which corresponds to the elutriating velocity, is proportional to the square of the radius, that is, to the extent of surface of the particles. If Bhatnagar's observations are correct it follows, therefore, that the magnitude of the charge present on the precipitating ion will determine the extent of surface of particles formed by coagulation of sols. Unfortunately, the experimental procedure is open to so many possible sources of error and the observations are so incomplete, that any deductions based on the recorded data would seem to be premature.

Colloidal copper ferrocyanide is precipitated by methyl alcohol in rather high concentration. Gurchot¹ suggests two possible explanations of this phenomenon: first, that the coagulation is brought about by a decrease in surface tension; and, second, that the negative charge on the particles is reduced below the critical value by the selective adsorption of alcohol. The second explanation is regarded as the more probable since surface tension decrease would tend to cause peptization rather than agglomeration. Gurchot implies that the reduction in the negative charge of the ferrocyanide particles is due to selective adsorption of the positive radical of the alcohol. Because of the slight polarity of the alcohol molecules, it seems likely that this effect will be negligible. A more probable explanation is that alcohol decreases the adsorption of the stabilizing ferrocyanide ion, either by displacing the latter or by cutting down the ionization of the salt in the intermicellar liquid.²

Copper ferrocyanide was at one time used as a pigment known as Hatchett's brown. Like the ferrocyanides of most of the

¹ *J. Phys. Chem.*, **30**, 99 (1926).

² For a fuller discussion of the effect of non-electrolytes on the stability of sols, see p. 46.

metals, the hydrous gel is a mordant more especially for basic dyes.¹ The black silver image in an ordinary photographic print may be converted into a red one, consisting in part of copper ferrocyanide, by immersing the print in a copper toning bath which is essentially a solution of copper ferrocyanide in an alkaline salt of citric, tartaric, or oxalic acid together with other salts.² Owing to the mordanting action of the ferrocyanide dye, toned images may be obtained by immersing the copper-toned print in an acid solution of a basic dye such as thioflavine, victoria green, methyl green, methylene blue, chrysoidine, or methyl violet.³

ZINC FERROCYANIDE

The gel and sol of zinc ferrocyanide are very similar to those of copper ferrocyanide in all respects except color, and may be obtained by the same procedures. The sol of the zinc salt has not been used extensively in the study of colloid chemical phenomena because it is not colored. For this reason, however, the gel has been used as a mordant more frequently than the highly colored copper salt. Color lakes suitable for printing on paper and textiles are obtained by mixing solutions of a basic dye and zinc sulfate, followed by the addition of a solution of sodium or potassium ferrocyanide.⁴ Zinc ferrocyanide is also employed in the direct printing of cotton fabrics. In the presence of ammonia, zinc salts do not precipitate zinc ferrocyanide from potassium ferrocyanide solution, unless the solution is boiled. It is therefore possible to incorporate both of these reagents with the printing dye instead of previously mordanting the fabric with ferrocyanide.⁵

The tendency of zinc ferrocyanide to adsorb potassium ferrocyanide interferes with the estimation of zinc by titration with ferrocyanide and with the estimation of ferrocyanide by titration with zinc ion. It is claimed that this difficulty can be avoided by adding an excess of potassium sulfate. The formula of the

¹ CLARK: Eastman Kodak Company, Abridged Publications, **2**, 130 (1915-16).

² FERGUSON: *Phot. J.*, 133 (1900).

³ CRABTREE: *J. Franklin Inst.*, **186**, 515 (1918).

⁴ JUSTIN-MUELLER: *Rev. gén. mat. color.*, **24**, 129 (1920).

⁵ PLANOVSKII and SMIRNOV: *Chem. Abstr.*, **18**, 1202 (1924).

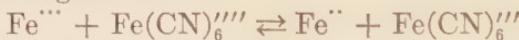
salt obtained by following a definite procedure is said to be $Zn_3K_2[Fe(CN)_6]_2$.¹ The solutions must be standardized against each other and it is recommended that titrations of an unknown be carried out as nearly as possible under the same conditions as the standardization. While the gelatinous precipitate may be a definite double salt of the above formula free from adsorbed ferrocyanide or zinc, the author thinks it unlikely that such is the case. The very fact that the titration of an unknown sample must be carried out under the same conditions as the standardization argues against the contention that the precipitated gel is a phase of unvarying composition.

¹ MEURICE: *Ann. chim. anal.*, **18**, 342 (1913).

CHAPTER XVI

PRUSSIAN BLUE

The most important of the iron cyanogen derivatives are the various blue hydrous substances comprised under the general names Prussian or Berlin blue and Turnbull's blue. The gels are obtained (1) by the interaction of ferric salts and ferrocyanides, (2) by the interaction of ferrous salts and ferricyanides, (3) by the oxidation of ferrous ferrocyanide, and (4) by the reduction of ferric ferricyanide. The freshman is usually told that the product of the first reaction is ferric ferrocyanide, $\text{Fe}^{+++}[\text{Fe}(\text{CN})_6]^{4-}$ or Prussian blue and the product of the second reaction is ferrous ferricyanide $\text{Fe}^{++}[\text{Fe}(\text{CN})_6]^{4-}$ or Turnbull's blue. It appears, however, that ferrous ferricyanide does not exist. On mixing either a ferric salt and a ferrocyanide or a ferrous salt and a ferricyanide the following equilibrium is set up before precipitation begins:



From the electrochemical data of Abegg,¹ the equilibrium constant of this reaction is found to be:

$$k = \frac{\text{Fe}^{+++} \cdot [\text{Fe}(\text{CN})_6]^{4-}}{\text{Fe}^{++} \cdot [\text{Fe}(\text{CN})_6]^{3-}} = 10^{-5}$$

Thus, the equilibrium appears to be strongly in favor of the formation of ferricyanide but this equilibrium is disturbed by the formation of a precipitate whose composition is determined by the solubility relations which exist. As a result of extended investigations, Hofmann² concludes that all the blue gels are ferrocyanides, derivatives of hydroferrocyanic acid in which the hydrogen is either wholly or partly replaced by ferric iron and partly by another metal. When alkali (X) ferro- or ferricyanides

¹ *Z. Elektrochem.*, **9**, 569 (1903).

² *Liebig's Ann.*, **337**, 1 (1904); **340**, 267; **342**, 364 (1905); **352**, 54 (1907); *J. prakt. Chem.*, [2] **80**, 150 (1909); cf., also, SKRAUP: *Liebig's Ann.*, **186**, 385 (1877); VORLÄNDER: *Ber.*, **46**, 181 (1913); BOWLES and HIRST: *J. Oil and Color Chem. Assoc.*, **9**, 153 (1926).

are employed the product is $\text{Fe}_4^{'''}[\text{Fe}(\text{CN})_6]_3^{''''}$ or $\text{XFe}^{'''}[\text{Fe}(\text{CN})_6]_3^{''''}$ or a mixture of the two. None of these compounds is obtained in any form other than as a hydrous gel except $\text{NH}_4\text{Fe}_3^{'''}[\text{Fe}(\text{CN})_6]_3^{''''}$ which may be prepared anhydrous and crystalline. The gels of the corresponding potassium and sodium salts are certain to be contaminated more or less by adsorption of alkali ferrocyanide. Müller added potassium ferrocyanide in gradually increasing proportions to ferric chloride and followed the course of the reaction both by indirect analysis of the precipitates¹ and by electrometric titration.² The following compounds appear to form in order $\text{Fe}_4^{'''}[\text{Fe}(\text{CN})_6]_3^{''''}$, $\text{K}_2\text{Fe}_2^{'''}[\text{Fe}(\text{CN})_6]_3^{''''}$, and $\text{K}_3\text{Fe}(\text{CN})_6$. When the ratio of FeCl_3 to $\text{K}_4\text{Fe}(\text{CN})_6$ is 4 or more to 3, the product is $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ but in other proportions, the product is a mixture of this compound with the complex salts. Similar observations on adding increasing amounts of $\text{K}_3\text{Fe}(\text{CN})_6$ to ferrous chloride indicate the formation of the following substances in order: $\text{K}\text{Fe}_2^{'''}\text{Fe}_5^{'''}[\text{Fe}(\text{CN})_6]_5^{''''}$, $\text{K}\text{Fe}^{'''}\text{Fe}_3^{'''}[\text{Fe}(\text{CN})_6]_3^{''''}$, $\text{K}\text{Fe}^{'''}[\text{Fe}(\text{CN})_6]^{''''}$ and $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$. Intermediate compositions are assumed to be mixtures. On the strength of these observations, Müller concludes with Hofmann that Prussian blue and Turnbull's blue are both ferrocyanides but unlike Hofmann, Müller insists that the two are not identical. He prefers to regard Prussian blue as essentially potassium ferric ferrocyanide $\text{K}\text{Fe}^{'''}\text{Fe}(\text{CN})_6^{''''}$ and Turnbull's blue as chiefly potassium ferrosoferric ferrocyanide $\text{K}\text{Fe}^{'''}\text{Fe}^{'''}[\text{Fe}(\text{CN})_6]_3$. Obviously, this distinction is purely arbitrary since the composition of the glue gel varies with the relative proportions of the reacting constituents. Moreover, from numerous analyses of blues, Tarugi³ claims that a percentage of oxygen is present in all of them that cannot be attributed to analytical errors. This result was confirmed in various ways with highly accurate analytical procedures and with reciprocal control. This is not at all surprising when the blue is made by the interaction of ferrocyanide and ferric chloride, since the iron salt is partly hydrolyzed giving colloidal hydrous ferric

¹ MÜLLER and STANISCH: *J. prakt. Chem.*, [2] **79**, 81; **80**, 153 (1909); **84**, 353 (1911); MÜLLER: *Ibid.*, **90**, 119 (1914).

² MÜLLER and LAUTERBACH: *J. prakt. Chem.*, [2] **104**, 241 (1922).

³ *Gazz. chim. ital.*, **55**, 951 (1925).

oxide which will be carried down by the gel. Indeed Vorländer¹ showed that this hydrolysis of ferric salts causes the reaction with ferrocyanide to proceed at a rate sufficiently slow to measure. In this connection, mention should be made of Reitstötter's² observation that the addition of a small amount of ferric salt to the test tube containing the precipitate thrown down from an alumina sol by the required amount of ferrocyanide, does not give Prussian blue until after an appreciable interval of time. This is due to the very strong adsorption of ferrocyanide by alumina which removes the former completely from the field of action. If another strongly adsorbed anion is added to the alumina either before or after coagulation, the ferrocyanide is displaced in part and the time required for the appearance of Prussian blue is diminished appreciably.

Since in all cases the precipitated blue gel is more or less impure, the author prefers to designate the mixture of salts by the general term Prussian blue and to discontinue the use of the term Turnbull's blue.

A brown sol of ferric ferricyanide is formed by the interaction of aqueous solutions of ferric chloride and potassium ferricyanide.³ Ultramicroscopic examination shows that the particles increase in size gradually and a green substance finally separates out. This green precipitate is probably a mixture of ferric ferricyanide and Prussian blue. A similar green substance is formed by adding ferric chloride to potassium ferricyanide solution containing a little potassium ferrocyanide. Williams⁴ believes the gel to be a double salt of ferric ferricyanide and potassium ferric ferrocyanide which he formulates $\text{Fe}_{29}^{\text{III}}\text{K}_3[\text{Fe}^{\text{II}}\text{Fe}_{27}^{\text{III}}(\text{CN})_{18}]_9 \cdot 210\text{H}_2\text{O}$. As is the case with so many alleged complex compounds, the gel in question is doubtless nothing more than a mixture which can have any composition you like, depending on how it is made.

Hydrous ferric oxide treated with hydrocyanic acid gives a black gel which is an irreversible adsorption complex of Prussian

¹ *Ber.*, **46**, 181 (1913); *Kolloid-Z.*, **22**, 103 (1918).

² *Kolloid-Z.*, **21**, 197 (1917); FREUNDLICH and REITSTÖTTER: *Ibid.*, **23**, 23 (1918); VORLÄNDER: *Ibid.*, **22**, 103 (1918).

³ HALLER: *Kolloid-Z.*, **20**, 76 (1917).

⁴ "The Chemistry, Manufacture, and Estimation of Cyanogen Compounds," 142 (1915).

blue and ferric oxide.¹ It is believed that the hydrocyanic acid first reduces some of the ferric oxide to ferrous oxide which dissolves in the excess acid to give ferrocyanic acid. The latter then reacts with hydrous ferric oxide giving Prussian blue which is adsorbed by the remaining oxide. A black gel containing as much as 10.5 per cent Prussian blue was prepared in this way.

While the work of Hofmann and Müller has gone a long way toward clearing up the chemistry of the complex iron-cyanogen compounds, there is still considerable doubt as to whether such alleged compounds as $KFe_2Fe_5[Fe(CN)_6]_5$ actually exist. One can not emphasize too strongly that the analysis of a gel, either by a direct or an indirect method, does not give sufficient data to establish the gel as a definite compound. Electrometric titrations, likewise, cannot give conclusive results when a gel with a strong adsorption capacity is precipitated during the process.

An interesting experiment in diffusion which involves the formation of Prussian blue, is Alexander's so-called "patriotic tube." A test tube is filled two-thirds full of a slightly alkaline agar sol containing enough phenolphthalein to turn it pink and a little potassium ferrocyanide. After the agar has set to a solid, a dilute solution of ferric chloride is carefully poured on top. The ferric ion forms with the ferrocyanide a slowly advancing band of blue before which the more rapidly diffusing hydrochloric acid spreads a white band as it discharges the pink color of the indicator. In a few days the tube is about equally banded in red, white, and blue.² Creighton³ obtained rhythmic bands of Prussian blue by passing an electric current through a dilute solution of potassium ferrocyanide and sodium chloride in an agar jelly contained in a tube 70 centimeters long and 2 centimeters in diameter.

Commercial Prussian blue is a very important blue pigment. What is said to be the finest variety, known as Paris blue, is obtained by mixing potassium ferrocyanide and ferrous sulfate, followed by oxidation of the white ferrous ferrocyanide by

¹ WEDEKIND and FISCHER: *Ber.*, **60 B**, 541 (1927); WEDEKIND: *Naturwissenschaften*, **15**, 163 (1927).

² Cf. HOLMES: "Laboratory Manual of Colloid Chemistry," 11 (1925).

³ *J. Am. Chem. Soc.* **36**, 2357 (1914).

chlorine.¹ The use of potassium salts is said to be of importance, the color being less satisfactory when sodium salts are employed. Eibner and Gerstacker² claim that blues with a high potassium content possesses the technically desirable greenish shade while those poor in potassium are dull with a violet tinge. It is not obvious why sodium salts should yield a pigment inferior in color to potassium salts. Since the variation in color is doubtless due to the physical character of the precipitate, there is no apparent reason why a proper control of the conditions of precipitation should not yield a satisfactory product with sodium salts. Williams³ claims that potassium salts may be replaced by ammonium salts with satisfactory results.

In commercial pigments, Prussian blue is diluted with starch, heavy spar, gypsum, zinc white, or burned and ground kaolin. The white constituent is first pulverized and then added to a paste of Prussian blue. The relative degree of subdivision of the white and colored constituents is quite important. If a very fine powder is shaken with a moderately coarse one, the former tends to coat the latter instead of filling the voids in the space occupied by the coarser material. In one experiment, Briggs⁴ mixed 0.032 gram of Prussian blue with 10 grams of dolomite which passed a 40-mesh sieve and did not pass a 100-mesh sieve; and in a second experiment, the same amount of Prussian blue was mixed with 10 grams of dolomite, all of which would pass a 200-mesh sieve. In the first case, the resulting mixture was a deep blue and in the second it was practically white although the percentage compositions were identical in the two cases.

PRUSSIAN BLUE SOLS

Prussian blue gel precipitated by a slight excess of ferrocyanide is called "soluble" Prussian blue because it is so readily peptized by washing.⁵ The gel formed in the presence of a slight excess of

¹ Cf. THORPE: "Dictionary of Applied Chemistry," **2**, 448 (1921).

² *J. Soc. Chem. Ind.*, **31**, 1041 (1912).

³ "The Chemistry, Manufacture, and Estimation of Cyanogen Compounds," 120 (1915).

⁴ *J. Phys. Chem.*, **22**, 216 (1918); cf. FINK: *Ibid.*, **21**, 32 (1917).

⁵ BERZELIUS: *Schweigg. J. Chem. Physik.*, **30**, 1, 34 (1820).

iron is not peptized easily by washing and so is designated "insoluble" Prussian blue. This term is a misnomer, since the so-called insoluble compound is carried into colloidal solution by thorough washing, preferably by the aid of the centrifuge, especially if a trace of potassium ferrocyanide is added to the wash water.¹ A sol is formed also by peptization of the gel with oxalic acid,² followed by dialysis. Unlike oxalic acid, the neutral oxalates of potassium, sodium, and ammonium dissolve the Prussian blue gel, giving a soluble potassium iron oxalate with a green color.³ Hence the test for ferric iron by the Prussian blue test loses its reliability in the presence of neutral oxalates. The oxalic acid sol was once employed as an ink but it has now been replaced by the blue aniline colors.

The addition of an excess of potassium ferrocyanide to a ferric chloride solution gives a blue-green to light-green sol⁴ which is not a definite green double salt or other compound. Instead, it is a mixture of very finely divided Prussian blue with a small amount of adsorbed colloidal hydrous ferric oxide. A similar green sol results on mixing a dilute sol of ferric oxide with Prussian blue. The addition of alcohol, hydrochloric acid, or neutral salts, including an excess of potassium ferrocyanide, to the green sol throws down the usual deep blue precipitate.

Prussian blue sols are composed of non-spherical particles⁵ which are negatively charged as a rule owing to preferential adsorption of ferrocyanide ion. Bachmann showed, however, that the particles are positively charged in the presence of a suitable small excess of the strongly adsorbed ferric ion. The behavior is thus analogous to that of the silver halides which assume a negative charge in the presence of excess halide ion and a positive charge in the presence of excess silver ion. The positive Prussian blue sol precipitates slowly on standing but is

¹ BACHMANN: *Z. anorg. Chem.*, **100**, 77 (1917).

² STEPHEN and NASH: *Ann. Pharm.*, **34**, 348 (1840); KARMBRACH: *J. prakt. Chem.*, **20**, 175 (1840); GRAHAM: *Phil. Trans.*, [1] **151**, 183 (1861); REINDEL: *J. prakt. Chem.*, **102**, 38, 255 (1867).

³ KOHN: *Monatsh.*, **43**, 373 (1923); KOHN and BENCZER: *Ibid.*, **44**, 97 (1923).

⁴ BACHMANN: *Z. anorg. Chem.*, **100**, 77 (1917).

⁵ SZEGVARI: *Z. physik. Chem.*, **112**, 277 (1924).

completely reprecipitated by shaking. The stability of the sols is increased by the presence of a small amount of gelatin.¹

Prussian blue sols are precipitated readily by electrolytes, especially those with multivalent cations. Pappadà² found the order of precipitating power to be: Fe, Al, Cr > Ba, Cd > Sr, Ca > H > Cs > Rb > K > Na > Li. Lachs and Lachman³ investigated the precipitating power of salts with cations of the same valence. The results are given in Table XXXVII. On the basis of these and similar observations on colloidal antimony

TABLE XXXVII.—COAGULATION OF COLLOIDAL PRUSSIAN BLUE BY ELECTROLYTES

Sol 1		Sol 2	
Electrolyte	Precipitation value, milliequivalents per liter	Electrolyte	Precipitation value, milliequivalents per liter
LiNO ₃	130	KNO ₃	80
KNO ₃	40	Mg(NO ₃) ₂	11.4
CsNO ₃	7	Ca(NO ₃) ₂	9.0
Li ₂ SO ₄	1000	Sr(NO ₃) ₂	5.8
K ₂ SO ₄	72	Ba(NO ₃) ₂	2.2
Cs ₂ SO ₄	7		

pentoxide, it is concluded that the adsorption of an ion which determines its precipitating power is closely related to its degree of hydration. According to Fajans,⁴ the hydration of an ion may be regarded as the formation around the ion of a polarized water envelope consisting of dipoles, the process being accompanied by a positive heat effect. From this point of view, one should expect the adsorption of the ions to be accompanied by partial dehydration, the extent of which will be determined by the heat of hydration of the ions. Since both the heat of hydration and the amount of hydration decreases in the series from

¹ LOBRY DE BRUYN: *Rec. trav. chim.*, **19**, 236 (1900).

² *Kolloid-Z.*, **6**, 83 (1911); cf. YAJNIK and BHATIA: *J. chim. phys.*, **22**, 589 (1925).

³ *Z. physik. Chem.*, **123**, 303 (1926).

⁴ FAJANS and BECKERATH: *Z. physik. Chem.*, **97**, 478 (1921).

lithium to caesium and from magnesium to barium, it follows that the adsorptive power and coagulative action should increase in this direction, as the results show.¹

In order to get a more exact insight into the relationship between adsorbability and heat of hydration, the heat of adsorption in solution, U_2 , can be regarded as the small difference between the heat of adsorption in vacuum, U_v , and the heat of hydration, W , that is, $U_2 = U_v - W$. According to Fajans² the heat of adsorption in vacuum is inversely proportional to the sum of the radius of the charged ions, r_1 , and of the adsorbed discharged ions, r_2 ; that is

$$U_v = \frac{K_1}{r_1 + r_2}$$

Born³ points out that the heat of hydration includes the dielectric constant of the solution and as a first approximation is inversely proportional to the ratio of the adsorbed ions r_2 ; that is

$$W = \frac{K_2}{r_2}$$

Now if K_1 , r_1 , and K_2 are assumed to be constant then

$$U_2 = \frac{K_1}{r_1 + r_2} - \frac{K_2}{r_2} = f(r_2)$$

On differentiation this becomes

$$f'(r_2) = -\frac{K_1}{(r_1 + r_2)^2} + \frac{K_2}{r_2^2} = \frac{K_2(r_1 + r_2)^2 - K_1 r_2^2}{r_2^2(r_1 + r_2)^2}$$

The last value comes out to be positive in the case under consideration. This means that although the two values $\frac{K_1}{r_1 + r_2}$ and $\frac{K_2}{r_2}$ decrease with increasing radius of the adsorbed ions r_2 , the difference with increasing r_2 is always positive. Accordingly, the heat of adsorption must increase in the ion series from lithium to caesium and from magnesium to barium. Some data on the heat of hydration of alkali cations and the heat of adsorption of the corresponding nitrates by charcoal are given in Table XXXVIII. It will be seen that the heat of hydration falls as

¹ WEISER: *J. Phys. Chem.*, **29**, 955 (1925); cf. p. 287.

² Verh. deutsch. physik. Ges., **21**, 549, 709, 714 (1919); *Naturwissenschaften*, **37**, 1 (1921).

³ Z. Physik, **1**, 47 (1920).

one goes down the series, while the heat of adsorption of LiNO_3 , NaNO_3 , and KNO_3 is in the ratio 8.9:10.4:11.7. Since the heat of adsorption is a measure of the adsorability, the increase in precipitating power from lithium to caesium is accounted for.

TABLE XXXVIII.—HEAT OF HYDRATION OF ALKALI IONS AND HEAT OF ADSORPTION OF ALKALI NITRATES ON CARBON

Heat of hydration of alkali ions		Molecular heat of adsorption of salts by carbon	
Ion	Heat of hydration, Calories per gram ion	Salt	Heat of adsorption per mol, relative values
Li.....	120	LiNO_3	8.90
Na.....	92	KNO_3	10.40
K.....	72	CsNO_3	11.72
Rb.....	68		
Cs.....	62		

While these considerations indicate the existence of a qualitative relationship between adsorption and heat of hydration in the cases under consideration, it should be emphasized that this factor is but one of a number of factors which determine adsorbability. Indeed, it is probable that heat of hydration of ions plays but a minor role in many instances. Thus we have seen that the solubility of the salt which an ion may form with an adsorbent appears to be the important factor in the adsorption of certain ions.¹

In this connection, Mukherjee² attributes the variation in adsorbability in a series of ions such as the alkalies, to differences in their mobilities. The ions adsorbed on the particles exert an attraction on the ions of opposite sign in the solution. The latter will be held firmly so that they cannot migrate provided their kinetic energy remains below a value U_2 which is necessary to separate the ion from the oppositely charged point of the surface. The value U_2 , as heretofore, is the work of adsorption or its equivalent, the heat of adsorption. According to Mukherjee, it can be calculated from the expression

$$U_2 = \frac{n_1 n_2 e^2}{Dx}$$

¹ Cf. p. 217.

² *Phil. Mag.*, [6] **44**, 321 (1922).

in which n_1 is the valence of the adsorbed ion, n_2 the valence of the ion of opposite charge in the solution, e the charge on the electron, D the dielectric constant of water, and x the distance between the centers of the ions at the position of minimum distance. The value of x is therefore equal to the sum of the radii of the ions or $(r_1 + r_2)$. Born¹ showed, however, that the radius of the alkali metals increases in the series from lithium to caesium; hence, the value of U_2 calculated from the above equation must decrease from lithium to caesium which is contrary to the observations of Lachs and Lachman. Moreover, the view of Mukherjee is unsound theoretically, since adsorption represents an equilibrium condition which would not be determined by the mobility of the ions.²

Mutual Action of Sols.—If one sol is treated with a second, the first will be stabilized, sensitized, or completely or partially precipitated, depending on the nature and relative concentrations of the two sols. Sol peptized by water such as gelatin usually exert a protective action on others and are therefore called protective colloids. Even in such cases, however, the charge and relative concentrations of the two sols determines whether or not stabilization takes place. Thus Billitzer³ found that gelatin in acid or neutral solution is a positive sol and so will agglomerate negative sols but not positive ones such as hydrous ferric oxide; whereas gelatin in ammoniacal solution is a negative sol and so precipitates hydrous ferric oxide. No precipitate is thrown down, however, if gelatin is first added to colloidal ferric oxide, followed by the addition of ammonia. In the latter case we get a stable mixture of positive sols changed simultaneously to a stable mixture of negative sols by the addition of hydroxyl ions.

If a small amount of a positively charged sol is added to a large amount of a negatively charged sol, the former may be stabilized owing to adsorption of the latter which, in turn, is sensitized to some extent. Complete mutual precipitation takes place when one sol has adsorbed the amount of another sol carrying an equivalent quantity of an ion of opposite charge. The addition of electrolytes to the mixture of sols will widen the range of

¹ *Z. Physik*, **1**, 221 (1920).

² Cf. ZSIGMONDY: "Kolloidchemie," 5th ed., 200 (1925).

³ *Z. physik. Chem.*, **51**, 148 (1905).

mutual precipitation. This is illustrated by some observations of Rabinerson¹ on the mutual action of positive hydrous ferric oxide sol and negative Prussian blue sol both in the absence and presence of sodium chloride. The behavior of the mixtures of sols whose compositions are given in Table XXXIX was investigated and the results shown graphically in Fig. 24. The percentage

TABLE XXXIX.—MIXTURES OF FERRIC OXIDE AND PRUSSIAN BLUE SOLS
WHOSE BEHAVIOR IS REPRESENTED IN FIG. 24

Number	Weight per 100 grams sol		Per cent	
	Ferric oxide	Prussian blue	Ferric oxide	Prussian blue
1	0.1	0.0025	97.56	2.44
2	0.1	0.0050	95.24	4.76
3	0.1	0.0100	90.91	9.09
4	0.1	0.0250	80.00	20.00
5	0.1	0.0500	66.67	33.33
6	0.050	0.0500	50.00	50.00
7	0.020	0.0500	28.57	71.43
8	0.010	0.0500	16.67	83.33
9	0.004	0.0500	7.41	92.59

composition of the mixtures is plotted as abscissa against the percentage amount of coagulation as ordinate. The several unbroken curves show the effect of sodium chloride in the amounts indicated on the mutual action of the sols. The dotted curves show the extent of coagulation by the sodium chloride of pure ferric oxide sols of the different concentrations. The ferric oxide sol is the more sensitive to the action of electrolytes, sodium chloride causing clouding of the 0.1 per cent sol at a concentration of 200 millimols per liter and complete coagulation at 500, while a 0.05 per cent Prussian blue sol requires 400 millimols per liter for clouding and 1000 for complete coagulation.

In the absence of sodium chloride, complete mutual precipitation takes place sharply with approximately 33 per cent ferric oxide and 67 per cent Prussian blue. Both to the right and left of this point the amount of precipitation falls off, decreasing to zero with about 90 per cent ferric oxide and 9 per cent Prussian

¹ *Kolloid-Z.*, 39, 112 (1926).

blue on the left, and with 28.5 per cent ferric oxide and 71 per cent Prussian blue on the right. The presence of sodium chloride

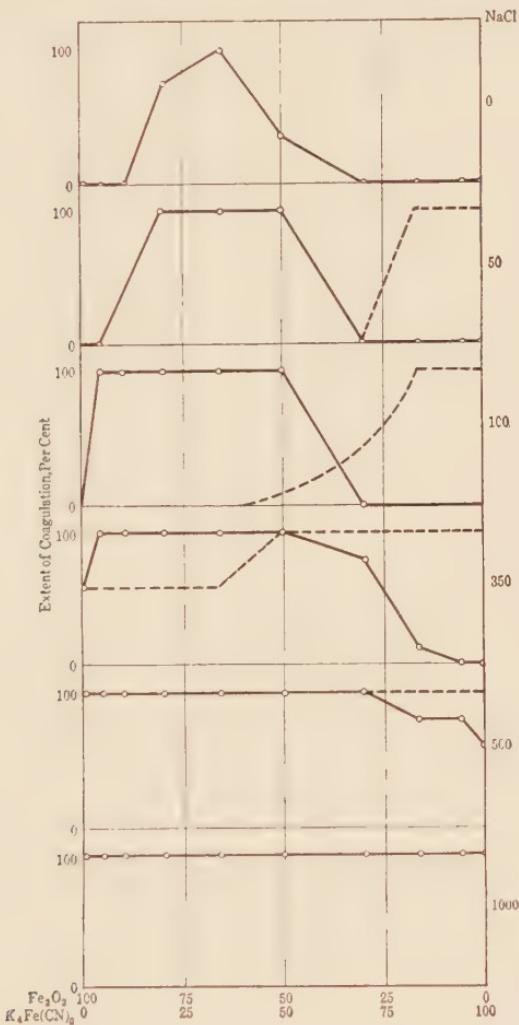


FIG. 24.—Mutual action of positive hydrous ferric oxide sol and negative Prussian blue sol, in the absence and in the presence of sodium chloride. (Sodium chloride concentration in milliequivalents per liter.)

in the mixture of sols increases the range of complete precipitation both to the left and to the right. This effect is more marked with excess ferric oxide than with excess Prussian blue since the former

sol is more sensitive to the action of sodium chloride. When the concentration of salt reaches 500 millimols per liter, the left portion of the curve becomes parallel with the abscissa while the right portion takes this position only after the concentration has been raised to 1000 millimols.

The observations show quite clearly the relationships among sensitization, mutual coagulation, and protective action. It is obvious that within a certain range each sol sensitizes the other since an amount of sodium chloride which will not coagulate either sol alone will effect complete coagulation of a mixture that appears stable. For example, the second and third mixture of sols listed in the table do not precipitate in the absence of sodium chloride but 100 millimols per liter will precipitate both mixtures although this amount of salt does not cloud either sol taken separately.

The protecting action of Prussian blue is also illustrated by the curves. For example, the dotted curves in IV disclose that the 0.1 per cent ferric oxide sol is clouded by 250 millimols per liter of sodium chloride whereas the 0.02 per cent sol is completely precipitated. On the other hand, the 0.02 per cent sol is not even rendered cloudy by this amount of salt when Prussian blue is present in the ratio of 71.4 per cent to 28.6 per cent of ferric oxide. In general, in the region of electrolyte concentration which lies between the coagulation value of the two sols of opposite sign, the more sensitive sol is protected by an excess of the more stable sol.

CHAPTER XVII

PERMEABILITY OF MEMBRANES—ULTRAFILTRATION— DIALYSIS

SEMIPERMEABLE MEMBRANES

A membrane is said to be semipermeable when it permits one constituent of a solution to pass through—usually water—and does not allow diffusion of the other constituents or one or more of the other constituents. The plasma membranes of cells are natural membranes of this kind. Traube¹ was the first to recognize a similar semipermeability in certain gelatinous precipitates, the so-called precipitation membranes of which copper ferrocyanide is the most familiar example. Such a membrane is obtained by holding a solution of copper sulfate in a glass tube which is subsequently immersed in a solution of potassium ferrocyanide. The film of copper ferrocyanide formed at the junction of the two solutions will allow water to pass through but not dissolved substances such as sugar and certain salts.

If a solution is covered with a layer of the pure solvent, diffusion of the dissolved substances takes place until the concentration throughout the system is the same. The force driving the dissolved substance from the more concentrated to the less concentrated solution until equilibrium is attained is termed osmotic pressure. The existence of this force may be demonstrated by placing a solution in a vessel with semipermeable walls closed except for a capillary tube, and immersing the vessel in pure solvent. Since the septum is, by definition, permeable to the solvent and impermeable to the solute and since equilibrium will be attained only when the concentrations on both sides are equal, it follows that the solvent must pass through the membrane and dilute the more concentrated solution. This manifests itself by a rise of liquid in the capillary tube. An unsupported

¹ *Archiv. Anat. Physiol.*, 86 (1867)

membrane of copper ferrocyanide ruptures so easily that it is not suitable even for qualitative observation of osmotic pressure. To get around this difficulty, Pfeffer¹ deposited the ferrocyanide on the inside of a porous cup by allowing the ions to diffuse into the supporting medium from opposite sides. A more satisfactory method devised by Morse² consists in driving the ions into the walls by means of an electric current. Membranes supported in this way have withstood pressures as high as 130 atmospheres and have proved to be nearly ideal as regards semipermeability.

Atomic Sieve Theory.—To account for the action of semipermeable membranes, Traube conceived of them as atomic or molecular sieves through which progressively larger molecules diffused with increasing difficulty. Thus a copper ferrocyanide membrane was believed to contain pores large enough for the small molecules of water to get through but too small to allow the larger sugar molecules to pass. This view was shown to be inadequate by the observations of Tammann,³ Walden,⁴ I. Traube,⁵ Barlow,⁶ and others⁷ who made comparative tests on a number of semipermeable membranes with a number of diffusing substances. If the action is that of a sieve, it should be possible to arrange the membranes in a series in the order of their permeability. On the contrary, it was found that a membrane quite impermeable to most substances may be more permeable to some than is a membrane which, in general, possesses high permeability. Moreover, the impermeability of a membrane such as rubber to water and its permeability to the much larger molecules of benzene and pyridine cannot be accounted for on the sieve theory. Finally, recent observations which will be reported in the next section furnish conclusive evidence that a membrane such as copper ferrocyanide is not a static system but

¹ "Osmotische Untersuchungen," Leipzig, (1877).

² Morse and his collaborators: *Am. Chem. J.*, **26**, 80 (1901); **28**, 1 (1902); **29**, 173 (1903); **34**, 1 (1905); **36**, 1, 39 (1906); **37**, 324, 425, 558; **38**, 175 (1907); **39**, 667; **40**, 1, 194, 266, 325 (1908); **41**, 1, 92, 257 (1909).

³ *Z. physik. Chem.*, **10**, 255 (1892).

⁴ *Z. physik. Chem.*, **10**, 699 (1892).

⁵ *Phil. Mag.*, [6] **8**, 704 (1904).

⁶ *Phil. Mag.*, [6] **10**, 1 (1905); FINDLAY and SHORT: *J. Chem. Soc.*, **87**, 819 (1905).

⁷ KAHLENBERG: *J. Phys. Chem.*, **10**, 169 (1906).

a dynamic one capable of undergoing reversible permeability under suitable conditions.

The Solution Theory. —The solution theory of the action of the semipermeable membrane postulates that a membrane is permeable to such substances as dissolve in it and impermeable to those that do not. This view was anticipated by Liebig¹ as early as 1848 when he said: "The volume changes of two miscible liquids which are separated from each other by a membrane depends upon the unequal wetting or attraction which the membrane exerts on the two liquids." The first experimental work with the object in view of testing this theory was carried out by L'hermite² in 1855. In a test tube he placed some water, above this a thin layer of castor oil, and above this a layer of alcohol. In the course of a few days the alcohol had passed through the castor oil to the water, leaving but two layers in the tube. Turpentine was substituted for the oil with the same results. Again, when a layer of chloroform was separated from a layer of ether by a layer of water, the ether passed through the water to the chloroform. As a result of similar observations on eight different combinations of this kind, L'hermite reached the conclusion that substances which pass through membranes first dissolve in them. This mechanism has been supported by the work of numerous investigators.³ Thus Kahlenberg found that benzene, toluene, and pyridine, which are soluble in rubber, diffuse through rubber, whereas water which is insoluble in rubber does not pass through. Moreover, trichloracetic acid passes through a rubber membrane when dissolved in benzene but only very slowly when dissolved in water. Kahlenberg assumes not only a solution of the liquids in membranes to which they are permeable but a kind of loose chemical union as well.

It has been shown that whether osmosis will take place in a given case or not depends upon the specific nature of the septum and the liquids that bathe it; and if osmosis does occur, these factors also determine the

¹ "Ursachen der Säftebewegung," Braunschweig, (1848); *Liebig's Ann.*, **121**, 78 (1862).

² *Ann. chim. phys.*, [3] **43**, 420 (1855).

³ GRAHAM: *Phil. Trans.*, **144**, 177 (1854); **151**, 183 (1861); NERNST: *Z. physik. Chem.*, **6**, 37 (1890); TAMMANN: *Ibid.*, **10**, 255 (1892); OVERTON: *Ibid.*, **22**, 189 (1897); BARLOW: *Phil. Mag.*, [6] **10**, 1 (1905); KAHLENBERG: *J. Phys. Chem.*, **10**, 169 (1906).

direction of the main current and the magnitude of the pressure developed. The motive force in osmotic processes lies in the specific attractions or affinities between the liquids used and also those between the latter and the septum employed. These attractors or affinities have also at times been termed the potential energy of solution, etc.; they are to the mind of the writer essentially the same as what is commonly termed chemical affinity.

While solution in the membrane may be a necessary and sufficient criterion for semipermeability in certain cases, Bigelow¹ and Bartell² demonstrated conclusively that osmotic effects can be obtained with inert materials where neither solution nor chemical reactions can take place. Thus porous cups served as semipermeable membranes when the pores were sufficiently fine or when they were clogged to a certain extent with such substances as barium sulfate, lead chromate, lead sulfate, etc. Moreover, finely divided materials such as silica, carbon, metallic copper, silver, and gold acted as semipermeable membranes when compressed into discs containing very fine pores. The limits of the pore diameters between which osmosis can take place are not definitely known but they undoubtedly vary from substance to substance. Bartell found the upper limit to be around 0.9 micron with unglazed porcelain clogged with various materials. This is, of course, much too large to represent the dimensions of molecular interstices which Traube believed to be essential for semipermeability in membranes.

The Adsorption Theory. The osmotic phenomena observed with a distinctly porous non-soluble membrane such as a clogged porous plate, is doubtless the result of negative adsorption as suggested by Mathieu³ and Nathansohn⁴ and emphasized by Tinker⁵ and Bancroft.⁶ If a solid adsorbent takes up relatively more of a solvent than of the dissolved substance, we have negative adsorption and the solution becomes more concentrated.

¹ *J. Am. Chem. Soc.*, **29**, 1576, 1675 (1907); **31**, 1194 (1909); BIGELOW and ROBINSON: *J. Phys. Chem.*, **22**, 99, 153 (1918).

² *J. Phys. Chem.*, **15**, 659 (1911); **16**, 318 (1912); *J. Am. Chem. Soc.*, **36**, 646 (1914); **38**, 1029, 1036 (1916).

³ *Ann. Physik.*, [4] **9**, 340 (1902).

⁴ *Jahrber. wiss. Botanik.*, **40**, 431 (1904).

⁵ *Proc. Roy. Soc. (London)* **92 A**, 357 (1916); **93 A**, 266 (1917).

⁶ *J. Phys. Chem.*, **21**, 441 (1917).

Mathieu observed this phenomenon with a number of solutions using porous plates, membranes, or capillary tubes as adsorbents. With normal solutions, the concentration in certain capillary tubes was found to be as low as one-tenth normal. The difference in concentration increases with decreasing radius of the capillary tubes and Mathieu concludes that with sufficiently fine capillaries, water alone would be adsorbed. The importance of this for the theory of semipermeable membranes was recognized especially by Bancroft.

If this conclusion is true and general, it accounts for the results of Bigelow and of Bartell, who found that osmotic phenomena appeared in porous cups when the pores were sufficiently fine or were clogged sufficiently. It is clear that we can get osmotic phenomena in two distinct ways, depending on whether we have a continuous film or a porous one. In the case of a continuous film, it is essential that the solvent shall dissolve in the membrane and that the solute shall not. Since the permeability is not dependent on adsorption, there is no reason why there should be any fundamental difference between the adsorption of a solute which does pass through the membrane and of one which does not pass through.

With a porous film we shall get osmotic phenomena only when the negative adsorption is so marked that the pore walls adsorb practically pure solvent and when the diameters of the pores are so small that the adsorbed film of pure solvent fills the pores full. There is, therefore, an important difference between a solute which does pass through a membrane having very fine pores and one which does not pass through, in that the first is adsorbed by the membrane and the second is not.

Since a gelatinous precipitate consists of myriads of particles enmeshed into a network which entrains liquid,¹ it is probable that copper ferrocyanide membranes are porous in the sense that a fine porous plate is porous and are semipermeable, therefore, because of strong negative adsorption. Tinker examined these artificial membranes microscopically and arrived at the conclusion that they are granular in character² with particles having diameters between 100 and 1000 $\mu\mu$. It is probable that the primary particles are much smaller than this and that what he was measuring was the diameter of secondary particles from partial agglomeration. In any event, it is difficult to see how

¹ Cf. WEISER: "The Hydrous Oxides," 13 (1926).

² Cf., also, GURCHOT: *J. Phys. Chem.*, **30**, 99 (1926).

even an approximate estimate of particle size could be arrived at from his published photographs. The important thing is that, independent of Mathieu, Nathansohn, or Bancroft, he concluded that negative adsorption in such a porous system is the primary cause of the semipermeability. In support of this view, he demonstrated that cane sugar which ordinarily does not diffuse through a copper ferrocyanide membrane is adsorbed negatively by the salt. Ten-gram samples of finely divided copper ferrocyanide were shaken with sugar solutions of various strengths and the change in concentration determined polarimetrically. From this, the amount of water adsorbed was calculated. The results with four samples dried in different ways and to different degrees are given in Table XL and shown graphically in Fig. 25. Correction was made for any water

TABLE XL.—ADSORPTION OF WATER FROM SUGAR SOLUTIONS BY $\text{Cu}_2\text{Fe}(\text{CN})_6$

Approximate strength of cane-sugar solutions, per cent	Water adsorbed by 100 grams of dry $\text{Cu}_2\text{Fe}(\text{CN})_6$			
	1 Dried completely in steam oven	2 Dried over H_2SO_4 , 10 grams contain 0.689 gram H_2O	3 Dried in air at 80° for 3 hours, 10 grams contain 1.38 grams H_2O	4 Not dried, 10 grams contain 3.14 grams H_2O
5	27.0	
10	18.2	23.9	22.7	24.5
20	15.0	22.5	20.1
40	13.4	18.0	22.2	20.0
60	13.2	14.7	20.8	14.0

present in the adsorbent before immersing in the solution. It will be seen that sample 3, which has been dried in air, adsorbs the most water and sample 1, which was completely dehydrated in a hot oven, adsorbs the least water. Complete dehydration is evidently accompanied by partial coalescence with consequent decrease in specific surface.

Tinker believes that the completely dried ferrocyanide first hydrates to $\text{Cu}_2\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ which continues to adsorb water. Since the amount of water in the compound appears to be determined entirely by the conditions of drying, it is probable that no definite hydrate exists. In any event, one may be pretty

certain that the gel is not a hydrous hydrate. It is known that alumina forms a definite trihydrate under certain conditions but alumina gel is a hydrous oxide and not hydrous trihydrate. So far as the theory of the semipermeable membrane is concerned, it is, of course, immaterial whether the salt is a hydrate or not.

Hartung¹ criticizes the view that semipermeability is the result of negative adsorption on the ground that potassium sulfate is adsorbed more strongly by copper ferrocyanide than potassium chloride and yet the chloride diffuses more readily than the sul-

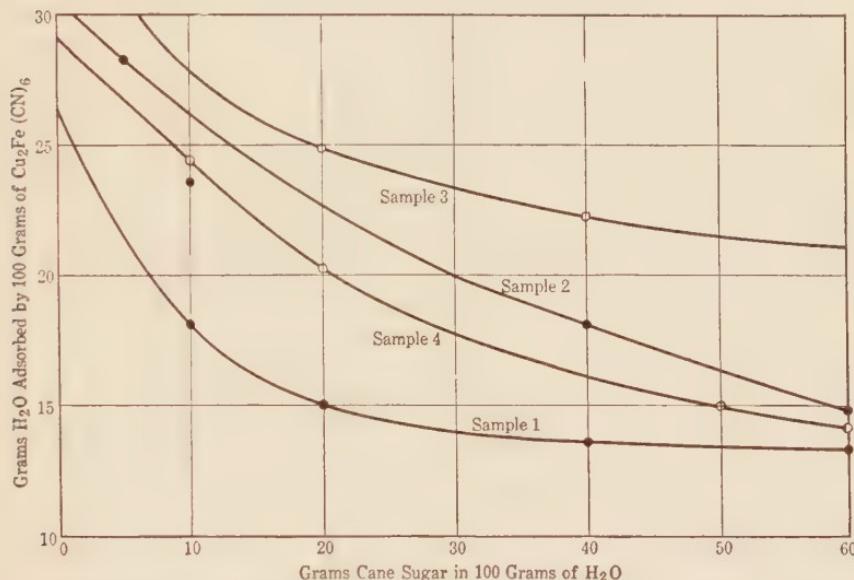


FIG. 25.—Adsorption of water from sugar solutions by copper ferrocyanide.

fate. In a later section² it will be shown that a membrane may be impermeable to an ion if the adsorption of the ion is almost irreversible and the resulting adsorption complex shows strong negative adsorption.

REVERSIBLE PERMEABILITY OF MEMBRANES

A porous membrane is semipermeable when it shows such strong negative adsorption that the pore walls adsorb practically pure solvent and when the diameters of the pores are so small

¹ *Trans. Faraday Soc.*, **15**, (3) 160 (1920).

² See p. 283.

that the adsorbed film completely fills them. The last specification is as important as the first; for if the adsorbed film does not completely fill the pores, the membrane will allow the solute to pass through the intervening capillaries. Since a copper ferrocyanide membrane in water is a negative colloidal film analogous to a sol, it follows that the presence of any solute contiguous to the membrane which causes it to undergo partial agglomeration, will increase its permeability. This is apparently what happens in a number of cases cited by Baneroff and Gurchot.¹ Thus Walden² found that tenth-normal solutions of thirty organic acids such as formic, acetic, propionic, butyric, valerianic, citric, and caproic, pass through copper ferrocyanide membranes whereas the sodium salts of the acids do not. It seems very unlikely that the difference in the behavior of acids and their sodium salts is due to solubility of the acids in the ferrocyanide membrane. It is much more probable that the negatively charged particles of the ferrocyanide membrane are aggregated, to a certain extent, by hydrogen ion rendering the membrane permeable. This is indicated by the following experiment: A copper ferrocyanide membrane supported by a thin layer of gelatin was formed in a glass tube 3 centimeters in diameter. When properly prepared, such membranes allowed no sugar to diffuse in at least 16 hours. On the inside of the tubes was placed a solution of sugar and acetic acid; and on the outside, a solution of blue litmus. After approximately 2 hours the litmus turned red and the outside solution was examined for sugar by Fehling's test. None was found when 0.2 per cent acetic acid was used, a mere trace with 0.5 per cent acid, and a moderate amount with 1.5 per cent acid. It is obvious that a suitable concentration of acid, either by its agglomerating action or in some other way, rendered the membrane sufficiently porous to allow sugar to pass through. The permeability of the membranes was not restored on washing to remove the excess acid.

Barlow³ found that alcohol likewise makes a copper ferrocyanide membrane permeable to sugar. Since sugar is insoluble in alcohol, this permeability cannot be due to increased solubility

¹ *J. Phys. Chem.*, **28**, 1279 (1924); **30**, 83 (1926).

² *Z. prakt. Chem.*, **10**, 705 (1892).

³ *Phil. Mag.*, [6] **10**, 1 (1905); **11**, 595 (1906).

of sugar in the membrane. Similarly, Czapek¹ observed the exosmosis of tannin from cells of *Echiveria* which were exposed to the action of various alcohols. The critical concentration for methyl alcohol was about 15 per cent; for ethyl, 10 to 11 per cent; for propyl, 4 to 5 per cent; for butyl, 1 to 2 per cent; and for amyl 0.5 per cent. Since the above solutions possess a surface tension about 68 per cent that for pure water, Czapek suggested that the surface tension lowering was responsible for the exosmosis. Since tannin is in colloidal solution, it is more likely that the exosmosis was due to partial coagulation of the cell membrane by the alcohols. In support of this view, Gurchot showed by means of a series of experiments similar to the one with acetic acid that copper ferrocyanide membranes are rendered permeable to sugar by suitable concentrations of the several alcohols.² Since a sol of copper ferrocyanide is precipitated by alcohol, it is reasonable to suppose that the dilute alcohol solutions in contact with the membranes cause partial agglomeration, giving pores so large that the film of adsorbed water does not fill them completely and so allows sugar to pass. Salts such as sodium chloride and calcium chloride likewise render the membranes permeable to sugar. The critical concentration was about 2 per cent for sodium chloride and below 1 per cent for calcium chloride which contains the more strongly adsorbed divalent ion. Below the critical concentration of the salts the latter will dissolve in the adsorbed water layer and will pass through the membrane by osmosis without coagulating it. But when the salt concentration is sufficiently high to neutralize the negative charge on the ferrocyanide below a critical value, partial agglomeration gives pores through which both the salts and sugar can pass by diffusion. When a dilute solution of copper sulfate was placed on one side of a membrane and of potassium ferrocyanide on the other side, the membrane did not become permeable to sugar in the presence of alcohol or salts, the membrane-forming reagents preventing the formation of effective pores. This observation suggested that a membrane rendered permeable to sugar by alcohols could be made impermeable once more by the addition of a suitable peptizing agent. Gurchot claims to have accom-

¹ *Ber. deut. botan. Ges.*, **28**, 159 (1910).

² Cf., also, SEN: *Quart. J. Indian Chem. Soc.*, **2**, 289 (1925).

plished this reversal by the use of copper sulfate. It was assumed that copper ion was the peptizing ion from analogy with the behavior of the silver halides; but since copper ferrocyanide is usually negative it is quite as likely that sulfate ion was the effective one. The observations of Hartung, to which reference was made earlier, indicate a relatively strong adsorption of sulfate by copper ferrocyanide.

While the permeability of a membrane will be increased by partial agglomeration and be restored by repeptization, it seems to me that such a mechanism need not be invoked in all cases to account for change in permeability. The degree of semipermeability in a given porous film is determined by the extent of the negative adsorption and the size of the pores. If the negative adsorption is not sufficiently marked or if the pores are too large, the latter will not be filled completely with the adsorbed film and so will be more or less permeable. Now it is altogether probable that the extent of the negative adsorption will be influenced by the magnitude and sign of the charge on the colloidal particles and the nature of any adsorbed ions. If this be true, it follows that the presence of electrolytes will influence the amount of the negative adsorption and so will change the permeability altogether apart from any agglomeration or peptization. The important thing, in any case, is that a membrane such as copper ferrocyanide is a dynamic system which varies in permeability with the nature of the surrounding medium and which is capable of reversible permeability under suitable conditions. Since it is fairly well established that the cell is surrounded by a semipermeable membrane comparable in certain respects to copper ferrocyanide, this concept enables one to account for a number of apparently contradictory facts in connection with the permeability of living cells.

The composition of the cell wall is not known nor is it known what makes it semipermeable let alone how the permeability is altered. There can be no doubt, however, that the cell, in pursuing its metabolic functions, does change its permeability in some way. Overton assumes that living cells are surrounded by a lipoid film. This in itself would account for a great many of the permeability phenomena but such a film would not let water through and it is known that water does get through.

Moreover, a great many acid dyes which are insoluble in lipoids penetrate certain cells readily. More striking still is the fact that the cells are normally impermeable to fruit sugar, cane sugar and other carbohydrates, the amino acids, the acid amides, and many other substances which are foodstuffs for the cells and must get into the cells from the outside. It is this condition which leads Höber¹ to remark: "What the cell can use it shuts out, and what it cannot use it lets in."

The only way to account for these apparently contradictory facts is to assume that the cell may be permeable to a given substance under certain conditions and impermeable under others. Collander² contends that protoplasm probably acts as an ultrafilter toward substances which are not soluble in lipoids; but in doing so he has neglected to distinguish clearly between a semipermeable membrane and an ultrafilter³ and has failed to take into account the important fact that cells are both permeable and impermeable to the same substance. Moreover, Collander reasons from analogy with the behavior of copper ferrocyanide membranes with the membrane-forming reagents on either side. He thus takes it for granted that cells always have the membrane-forming reagents on either side of them. This assumption is probably erroneous; in any event, it goes well beyond our present knowledge. Gurchot⁴ says:

On the other hand, coagulation of the membrane and a reversal of the same explain a great many things, even though the structural character of the membrane is still a puzzle. The objection to Overton's lipoid theory was that water-soluble substances like sugar could not penetrate a lipoid membrane. If, however, we assume the presence of a granular lipoid membrane analogous to copper ferrocyanide, in other words with each solid fat particle, or group of particles, surrounded with an adsorbed film of water supported in a separate pellicle, which is known to be present, we have essentially the same sort of thing as the copper ferrocyanide membrane and there seems to be no reason why, should such a membrane exist actually, it should not exhibit coagulation changes when necessary and allow, for example, sugar to enter the cell

¹ "Physikalische Chemie der Zelle und Gewebe," 5th ed. Part I, 503 (1922).

² *Kolloidchem. Beihefte*, **19**, 72 (1924); **20**, 273 (1925).

³ See p. 274.

⁴ *J. Phys. Chem.*, **30**, 103 (1926).

at one time and not at another. We have still to account, however, for the entrance of lipoid solvents through such a membrane. This is not at all a hopeless endeavor. Mention was made above of a film of adsorbed water surrounding the lipoid particles. It need not be that necessarily. The film could be a solution possessing properties analogous to a pyridine solution. In other words, it might dissolve substances other than and in addition to lipoid solvents. In this way the lipoid particles would be available as carriers for substances like ether and chloroform. Such a membrane would have the advantage of manifesting osmotic pressure, unlike an emulsion, and also to exhibit permeability changes in localized areas of the cell surface. It must be understood that only a very generalized picture of the cell membrane is attempted. Undoubtedly, membranes must differ with the functions of the particular organs of which they form a part. It may be objected that a substance like pyridine which may dissolve lipoid solvents may also dissolve the lipoid portion of the membrane and so destroy it. This need not follow at all. Pyridine itself is soluble in rubber, but it has been used with rubber membranes successfully by Kahlenberg without the rubber being damaged, even in boiling pyridine. On the other hand, if the idea of a discontinuous membrane, that is, a fine-grained one, with adsorbed water around the particles is not an attractive one we can postulate the existence of a continuous lipoid film of some sort which acts ordinarily as a semipermeable membrane, allowing only such things to go through which dissolve in it. A change in the surface tension of the surrounding medium might coagulate such a membrane into solid or semisolid drops and allow water-soluble substances to pass through. Such a membrane could be reversed by changing the surface tension of the surrounding medium, perhaps, in addition to the extraction of the coagulating agent from between the particles by the presence of a suitable solvent or reagent. The coagulating agent might be a water-soluble soap resulting from the reaction between sodium chloride and some fatty compound. This soap would reduce the surface tension of the solid film and pores would be formed between the solid drops in the membrane. The presence of calcium chloride would form a water-insoluble, inert, calcium soap which would dissolve in the membrane and subsequently would be decomposed by the cell after an increase in the surface tension of the external medium reversed the membrane and made it once more continuous. Clowes was not far away from such an explanation but he insisted that the cell must be an emulsion.¹

¹ See p. 308 of this volume.

ULTRAFILTRATION

A filter is a porous diaphragm by means of which solid particles in suspension may be separated from liquids. The pores in an ordinary filter are too coarse to remove colloidal particles but a filter may be made with pores sufficiently fine to screen out colloidal matter. Such a filtering medium is called an ultrafilter. The first systematic investigations on ultrafiltration were carried out by Bechhold¹ who employed strong filter paper that was impregnated either with gelatin hardened by formaldehyde or with collodion treated with acetic acid. The size of the pores in the filtering films were varied by using impregnating solutions of different concentrations.

It is possible to prepare an ultrafilter with pores sufficiently fine to retain suspended particles of most sols. Mixtures of two sols with particles of different sizes can be separated by a suitable ultrafilter provided neither colloidal substance adsorbs the other. Thus, Bechhold separated the muddy green mixture of colloidal Prussian blue and haemoglobin into its constituents, the finely divided red haemoglobin going through and the coarser Prussian blue remaining on the filter. The addition of sodium "lysalbinate," a protective colloid, to Prussian blue peptizes the latter so that it will pass through a filter which just stopped it before. If either colloidal ferric oxide or arsenic trisulfide is mixed with Prussian blue, adsorption takes place and everything is retained by the filter. The ultrafilter may be employed to

TABLE XLI.—ORDER OF PARTICLE SIZE IN SOLS FROM ULTRAFILTRATION EXPERIMENTS (BECHHOLD)

Coarse suspensions	1 per cent gelatin
Prussian blue	1 per cent haemoglobin
Platinum sols (Bredig)	Serum albumin
Hydrous ferric oxide	Diphtheria toxin
Casein	Protalbumes
Arsenic trisulfide	Hydrous silica
Gold (about $40\mu\mu$)	Lysalbinic acid
Bismuth oxide (Paal)	Duteroalbumoses
Lysargin (Paal's silver)	Litmus
Collargol (Silver, about $20\mu\mu$)	Dextrin
Gold	Crystalloids

¹ Z. physik. Chem., 60, 257 (1907); cf., also, MALFITANO: Compt. rend., 139, 1221 (1904).

separate certain of the decomposition products of the proteids. Thus by a suitable filter, protalumoses are separated from duteroalbumoses, the latter going into the filtrate. In Table XLI is given a list of substances arranged by Bechhold in decreasing order of particle size as determined by ultrafiltration experiments. Since it is well known that sols of the same substance can be made with particles of widely different sizes, it follows that the order given in the table holds only for the particular preparations with which Bechhold worked.

Distinction between an Ultrafilter and a Semipermeable Membrane.—The question naturally arises as to what is the difference, if any, between an ultrafilter and a semipermeable membrane. We have seen that a semipermeable membrane is a continuous film in which the solvent will dissolve but not the solute, or a finely porous membrane exhibiting such marked negative adsorption that the pore walls are covered with a film of pure solvent which completely fills the pores. Accordingly, a semipermeable membrane acts like a solvent and not like a sieve, irrespective of whether it is a continuous film like rubber or a porous one like a clogged porous plate or copper ferrocyanide. An ultrafilter, on the other hand, is merely a filter or a sieve with fine pores. The essential difference between a porous semipermeable membrane and an ultrafilter is that the latter shows no negative adsorption at all or so little negative adsorption that it does not prevent the membrane from acting like a sieve. Fortunately, Bechhold used in his ultrafiltration experiments a material which exhibited so little negative adsorption that it did not change to a semipermeable membrane at any pore diameter employed.¹

The recognition of a fundamental distinction between a semipermeable membrane and an ultrafilter enabled Bancroft² to set down a definite criterion for distinguishing a true solution from a colloidal solution. As a rule, this distinction can be made by applying the Gibbs' criterion for the presence or absence of a second phase. According to Gibbs, an apparent phase is not a one-phase system unless the properties are definitely defined when the temperature, pressure, and concentration are fixed. By

¹ See, however, p. 276.

² *J. Phys. Chem.*, **29**, 966 (1925).

applying this test, it may be shown readily that most colloidal solutions are two-phase systems. The difficulty comes with solutions of such substances as tannin and soaps which appear to satisfy Gibbs' criterion for a one-phase system when, in reality, they are two-phase systems. A similar situation is encountered with a mixture of two gases which in the last analysis is neither physically nor chemically homogeneous but which is a one-phase system, nevertheless. To take care of these cases, Bancroft assumes that any gas or vapor will pass through any pore through which any other gas or vapor will pass; in other words, that there is no such thing as a molecular sieve for gases, vapors, or liquids. If this unproved but reasonable assumption is granted, it leads directly to the conclusion that any substance which can be filtered out by an ultrafilter as defined above, is in colloidal solution. This criterion puts soap¹ and tannin in the list of colloidal solutions where they belong and will undoubtedly take care of highly dispersed solutions of such substances as molybdenum trioxide and molybdenum blue.² It should be pointed out, however, that any apparent solution which will pass through the finest ultrafilter that can be prepared in the laboratory, is not necessarily in true solution.

Before any distinction was made between a semipermeable membrane and an ultrafilter, people claimed that the failure to pass an ultrafilter did not serve to distinguish between a true and colloidal solution since sugar does not pass a copper ferrocyanide membrane and everybody recognizes that sugar is in true solution. This exception disappears since we now know that the mechanism of the action of an ultrafilter such as collodion is fundamentally different from the action of a semipermeable membrane such as copper ferrocyanide. Such cases as the impermeability of copper ferrocyanide membrane to ferrocyanide ion will be considered in the section on Donnan's theory of membrane equilibria.

While collodion membranes are usually permeable to dissolved substances, Michaelis³ claims to get what he calls molecular-

¹ McBAIN and JENKINS: *J. Chem. Soc.*, **121**, 2325 (1922).

² Cf. WEISER: "The Hydrous Oxides," 285 (1926).

³ Colloid Symposium Monograph, **5**, 135 (1927); *J. Gen. Physiol.*, **8**, 33 (1925); MICHAELIS and PERLZWEIG: *Ibid.*, **10**, 575 (1927); MICHAELIS and FUJITA: *Biochem. Z.*, **141**, 47 (1925); MICHAELIS, ELLSWORTH, and WEECH: *J. Gen. Physiol.*, **10**, 671 (1927).

sieve membranes by evaporating practically all of the organic solvent in which the collodion is dispersed instead of evaporating a part of the liquid and then immersing in water.

The diffusion of such a simple electrolyte as potassium chloride across a dried collodion membrane into pure water goes on with an extreme slowness which is surprising even compared with the diffusion of a non-electrolyte of comparable molecular size. With good membranes no traces of the electrolyte can be detected in the water even after days. The diffusion of potassium chloride is much accelerated if a solution of sodium nitrate is placed outside the membrane instead of pure water. At least the diffusion of potassium proceeds with a reasonable speed, whereas the diffusion of the chlorine is extremely slow, even in this case. This observation leads to the conclusion that the diffusibility of the cation is much greater than that of the anion, so that a reasonable speed of diffusion can take place only when the cation can be exchanged for another cation migrating in the opposite direction.

In classifying dried collodion as a molecular-sieve membrane, Michaelis is merely putting the very fine-pored collodion in the same category as copper ferrocyanide which he believes to be a molecular-sieve membrane. It seems fairly obvious, however, that the dried collodion is not acting like a sieve toward a potassium chloride solution any more than copper ferrocyanide acts like a sieve toward a sugar solution. For if the collodion is a molecular sieve it is difficult to account for its permeability to a non-electrolyte similar in molecular size to potassium chloride. Moreover, a sieve which allows potassium ion to pass would hardly prevent the passage of chloride ion which is almost identical in size. It is much more likely that collodion exhibits some negative adsorption for chloride ion just as sugar is adsorbed negatively by copper ferrocyanide. In the first case, the negative adsorption is insufficient to prevent free diffusion through the pores of ordinary collodion but is enough to inhibit or prevent diffusion through the much smaller pores of dried collodion. In other words, a collodion membrane is usually an ultrafilter but it may become a semipermeable membrane for certain substances if the pores are sufficiently fine. In accord with this view, Grollman¹ showed that the sieve-like action of ordinary

¹ *J. Gen. Physiol.*, **9**, 813 (1926).

collodion membranes is influenced by a layer of adsorbed liquid on the pore walls.

In view of the tendency of water to flow through a copper ferrocyanide membrane to dilute a sugar solution, it is clear that no liquid water can be filtered through it from a sugar solution unless the hydrostatic pressure of the latter is greater than the osmotic pressure. Furthermore, water will evaporate through such a membrane only in case the partial pressure of the water vapor in equilibrium with the solution is greater than the partial pressure of the water vapor outside. An interesting example of this, recalled by Baneroff,¹ is the behavior of certain molasses puncheons stored for more than 2 years in a damp cellar in London. Not only did no liquid water come out of them but in many instances water vapor passed into them until the casks burst from the resulting pressure.²

Since it is advantageous in practice as well as in theory to avoid identifying semipermeable membranes with ultrafilters, the choice of material for an ultrafilter must be limited to substances which show little or no selective adsorption for the solvent. Collodion serves as a fairly satisfactory ultrafilter for aqueous sols although, as already noted, the sieve-like action is affected by a variable layer of adsorbed fluid on the walls of the pores.³ Manning⁴ prepared nickel membranes by electroplating a film on bronze or nickel gauze. Such membranes have the advantage of being usable at high temperatures and with solvents that will attack the usual membranes. Manning's finest membranes contained pores 50 to $80\mu\mu$ in diameter. They were used to ultrafilter such colloids as silver in stearic acid, arsenic trisulfide, hydrous ferric oxide, cellulose acetate in acetone-water, sodium stearate in water, casein, etc. Gelatin from a 1 per cent solution was filtered out almost completely at 16° but at 45° the more highly dispersed sol passed through the pores. Cellophane furnishes a ready-made ultrafilter material which we have found invaluable in laboratory work in colloid chemistry.

¹ *J. Phys. Chem.*, **18**, 67 (1914).

² FERGUSON: *J. Chem. Soc.*, **6**, 122 (1854).

³ GROLLMAN: *J. Gen. Physiol.*, **9**, 813 (1926).

⁴ *J. Chem. Soc.*, **129**, 1127 (1926).

Ultrafiltration apparatus has been described for use in analytical chemistry,¹ for micro-ultrafiltration,² and for filtration at low pressures³ and at very high pressures.⁴ Hele-Shaw⁵ describes a modified form of the ultrafilter: A number of sheets of thin paper impervious to the liquid to be filtered are embossed on the surface so as to make channels, put into a pile, and punched with vertical holes. When put under pressure the liquid to be filtered goes down through the holes and comes out between the sheets. At sufficiently high pressure, the distance between the sheets can be made small enough for the sheets to act as an ultrafilter. Attempts to use this filter for commercial ultrafiltration have not been successful in this country.⁶

DIALYSIS

Dialyzing membranes, first used by Graham, are porous diaphragms which act like a sieve, allowing the passage of substances in true solution but holding back colloidal particles. An ultrafilter is thus a special form of the dialysis membrane.

The dialyzing apparatus described by Graham consists essentially of a wide cylindrical tube closed with parchment paper which is filled with the sol to be dialyzed and immersed in a larger vessel containing the dialysate, distilled water in the case of hydrosols. The diffusible material in the sol passes through the membrane into the water which is changed at intervals. Graham employed parchment paper as the dialytic septum but gold beaters skin,⁷ fish bladder,⁸ collodion,⁹ and cellophane may be used to greater advantage in certain cases. The dialysis is more rapid and thorough when the surface of the

¹ ZSIGMONDY and BACHMANN: *Z. anorg. Chem.*, **103**, 119 (1918); ZSIGMONDY and JANDER: *Z. anal. Chem.*, **58**, 241 (1919); JANDER and STUHLMANN: *Ibid.*, **60**, 289 (1921).

² THIESSEN: *Biochem. Z.*, **140**, 457 (1923).

³ ZSIGMONDY: *Z. angew. Chem.*, **26**, 447 (1913); SCHOEP: *Bull. soc. chim. Belg.*, **24**, 354 (1910); *Kolloid-Z.*, **8**, 80 (1911).

⁴ BECHHOLD and GUTLOHN: *Z. angew. Chem.*, **37**, 494 (1924); BRUNKER and OVERBECK: *Kolloid-Z.* (*Zsigmondy Festschrift*) **36**, 193 (1925).

⁵ *Proc. Roy. Soc. (London)* **103 A**, 556 (1923).

⁶ Cf. BANCROFT: "Applied Colloid Chemistry," 223 (1926).

⁷ ZOTT: *Wied. Ann.*, **27**, 229 (1886).

⁸ BANCROFT: "Applied Colloid Chemistry," 223 (1926).

⁹ ZSIGMONDY and HEYER: *Z. anorg. Chem.*, **68**, 169 (1910).

diaphragm is as large as possible compared to the volume of the sol. This has led to the use of parchment tubes and parchment or collodion thimbles of varying sizes depending on the amount of sol to be dialyzed. It is common practice to fold sheets of parchment or cellophane into a bag which will give a large amount of dialyzing surface for a given capacity.¹

Since the speed of dialysis is greater the larger the difference in concentration of the diffusible material on the two sides of the septum, it is advantageous to change the dialysate continuously. Provision is made for this in the so-called "star dialyzer" described by Zsigmondy and Heyer.² The apparatus consists of a round plate of ebonite with a hole in the middle from which ribs spread out radially to an edge which runs around the plate. Upon this edge fits an ebonite ring to which the collodion membrane is attached, the dish thus formed resting upon the radial ribs between the edge of the plate and the ring. The sol is contained in the dish, the membrane bottom of which is bathed by the external liquid which streams continuously through the middle hole and passes out through openings in the edge. A simpler apparatus for continuous dialysis is described by Neidle.³ It is essentially a bag of parchment paper or cellophane partially filled with water and suspended in a beaker containing the sol to be dialyzed. Distilled water is run at a fairly constant rate into the bag which is maintained a little more than half full by means of an automatic siphon. If the sol is stable when heated, the rate of dialysis may be increased enormously by raising the temperature. Thus, a purer chromic oxide sol was obtained by 10 hours' dialysis in a Neidle apparatus at the boiling point than resulted from 73 days' dialysis in the cold.⁴

Unfortunately, many sols cannot be dialyzed in the hot; but the rate of dialysis may be augmented by moving the liquid, the membrane, or both. Thus Thoms⁵ places the liquid to be dialyzed and the external liquid in hemispherical glass vessels pressed together at ground edges between which the membrane

¹ Cf. ERLACH and PAULI: *Kolloid-Z.*, **34**, 213 (1924).

² *Z. anorg. Chem.*, **68**, 169 (1910).

³ *J. Am. Chem. Soc.*, **38**, 1270 (1916).

⁴ NEIDLE and BARAB: *J. Am. Chem. Soc.*, **39**, 71 (1917).

⁵ *Ber.*, **50**, 1235 (1917); **51**, 42 (1918).

lies. The entire apparatus is turned either about an axis lying in the plane of the membrane or about one at right angles to it. What appears to be the most rapid device for dialysis in the cold is described by Gutbier, Huber, and Schieber.¹ In their appara-

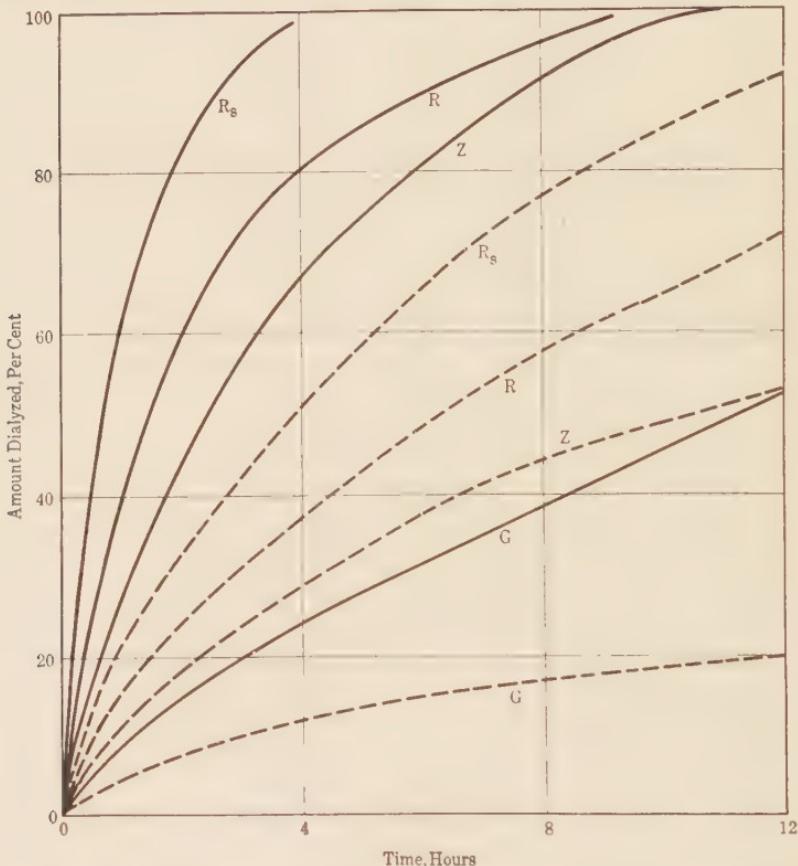


FIG. 26.—Rate of dialysis of 0.1 normal hydrochloric acid (unbroken curves) and of 0.1 normal sodium carbonate (dotted curves) with different types of dialyzers.

tus the membrane is placed around a cylindrical glass framework inside of which is a glass stirrer. The sol or solution to be dialyzed is placed inside the cell which is within but supported free from the vessel containing the dialyzing liquid. During dialysis the stirrer and parchment are rotated in opposite direc-

¹ Ber., 55 B, 1518 (1923); Chem. Ztg., 47, 109 (1923).

tions while the solvent liquid is changed continuously, entering at the bottom of the container and flowing out through a siphon at the top. Some comparative results with this apparatus and other dialyzers are shown graphically in Fig. 26. The percentage of the material dialyzed out is plotted against the time. The solutions in the cell in successive tests are 0.1 normal hydrochloric acid and 0.1 normal sodium carbonate. The 5 liters of water constituting the outer liquid of the Graham dialyzer (*G*) was changed every 3 hours. In the star dialyzer (*Z*) the water was allowed to run at the rate of 6 liters per hour. The rapid dialyzer contained 2.5 liters of water, and 6 liters per hour was flowed through without stirring (*R*) or with stirring (*R_s*). The advantage of stirring both the dialyzing solution and the dialysate is evidenced by these observations.¹

Since ultrafiltration and dialysis are related processes, it is not surprising to find an apparatus described which combines both operations.² A more common type of apparatus for purifying sols combines dialysis with electrolysis and electroendosmose. In the so-called electro-dialyzers³ the sol is contained in the inner compartment of a three-compartment vessel enclosed between diaphragm walls which prevent the passage of the colloidal particles. Electrodes are placed in the water contained in the two outer compartments and a suitable potential applied. Electrolytes are forced through the pores by electro-osmosis and the ions are forced through by electrolysis. If necessary, water is allowed to flow at the proper rate into the sol and also the electrode compartments. Since diaphragms which assume a negative charge hinder the passage of anions and those which assume a positive charge that of the cations, it is advisable, if practicable, to use two different kinds of diaphragm, negative at the cathode side and positive at the anode side.⁴

¹ Cf., also, ASTRUC and CANALS: *J. pharm. chim.*, [8] **2**, 14 (1925).

² WEGELIN: *Kolloid-Z.*, **18**, 225 (1916).

³ MORSE and PIERCE: *Z. physik. Chem.*, **45**, 589 (1903); RUBBEP: *Ber. deutsch pharm. Ges.*, **30**, 314 (1920); FOSTER and SCHMIDT: *J. Biol. Chem.*, **56**, 545 (1923); HOFFMAN and GORTNER: *Ibid.*, **65**, 371 (1925); MATTSON: *J. Agr. Research*, **33**, 553 (1926); DIERE: *Bull. soc. chim. biol.*, **8**, 144 (1926); ETTISCH and BECK: *Biochem. Z.*, **171**, 443, 454 (1926).

⁴ Cf., however, REINER: *Kolloid-Z.*, **40**, 123 (1926).

DONNAN'S THEORY OF MEMBRANE EQUILIBRIA

Donnan's theory of membrane equilibria deals with the equilibria resulting when a membrane separates two electrolytes containing one ion which cannot diffuse through the membrane. If one starts with two completely ionized electrolytes, NaCl and NaR, separated by a membrane impermeable to the ion R , Donnan showed that equilibrium will be established only when the product of the concentration of sodium and chloride ions has the same value on both sides of the membrane, thus

$$[\text{Na}^+]_1 \times [\text{Cl}']_1 = [\text{Na}^+]_2 \times [\text{Cl}']_2$$

where $[\text{Na}^+]_1$ and $[\text{Cl}']_1$ are the molar concentrations of sodium and chloride ions on one side of the membrane and $[\text{Na}^+]_2$ and $[\text{Cl}']_2$ the corresponding concentrations on the opposite side of the membrane. When equilibrium is reached, if the concentrations in one solution are $x\text{Na}$ and $x\text{Cl}$ and in the other $(y + z)\text{Na}$, $y\text{Cl}$, and zR , the equation of products becomes

$$x_2 = y(y + z)$$

It is obvious that x must be greater than y so long as z has a finite value, hence the concentration of chloride ion in the first solution must be greater than in the second, while the concentration of sodium ion must be greater in the second, than in the first. This gives rise to a potential difference E across the membrane which is represented by the equation

$$E = \frac{RT}{F} \log \frac{x}{y}$$

in which R is the gas constant, T the absolute temperature, and F the faraday.

The accuracy of these deductions has been established by investigations on a number of systems, for example, (1) with solutions of potassium chloride and lithium chloride using a layer of amyl alcohol as a membrane;¹ (2) with solutions of potassium and sodium chloride and potassium and sodium ferrocyanide, respectively, using a copper ferrocyanide membrane;² and (3) with solutions of Congo red and sodium chloride

¹ DONNAN and HARRIS: *J. Chem. Soc.*, **99**, 1554 (1911).

² DONNAN and ALLMAND: *J. Chem. Soc.*, **105**, 1941 (1914); DONNAN and GARNER: *Ibid.*, **115**, 1313 (1919); KAMEYAMA: *Phil. Mag.*, **50**, 849 (1925).

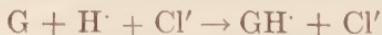
using a parchment membrane.¹ It is of interest to inquire into the nature of the action of the membrane in each instance. In the first case, the amyl alcohol acts as a non-porous semipermeable membrane in which the lithium chloride dissolves and passes through while the potassium chloride does not. In the second case, the ferrocyanide ion does not pass through the ferrocyanide membrane; but the reason is not obvious. If Baneroff is right in his contention that there is no such thing as a molecular sieve for substances in true solution, then the ferrocyanide membrane cannot be functioning as an ultrafilter or dialyzing membrane which screens out the ferrocyanide ion. As has been pointed out, the semipermeability of the ferrocyanide membrane toward a sugar solution is the result of strong negative adsorption of sugar. At the outset this appeared inadequate to account for the alleged impermeability to ferrocyanide ion which is adsorbed sufficiently strongly by copper ferrocyanide to peptize the gel as a stable negative sol. Donnan's observations suggest two possibilities: First, the strong positive adsorption of ferrocyanide ion may account for its failure to pass the membrane, equilibrium being established between the potassium and chloride ions in the system before sufficient amount of the larger ferrocyanide ions have diffused into the negatively charged gel to exceed the adsorption capacity of the gel. In line with this view, it was found that ferrocyanide passed through the membrane when the salt concentration was above 0.5 normal even though osmotic equilibrium was maintained by the addition of a suitable amount of sugar to the solution on the opposite side of the septum. This suggests the second possibility, that the alleged impermeability of the membrane to ferrocyanide ion does not exist, even with relatively dilute solutions. As this volume goes to press it has been found that neither of the above possibilities is correct. No ferrocyanide ion diffused through a certain ferrocyanide membrane into an isotonic sugar solution when the concentration was below 1.0 normal and slightly alkaline water only, was forced through a copper ferrocyanide ultrafilter from dilute solutions of potassium ferrocyanide. The explanation of this behavior is that copper ferrocyanide gel always contains adsorbed alkali ferrocyanide (Chap. XVI) which is retained so tenaciously

¹ DONNAN and HARRIS: *J. Chem. Soc.*, **99**, 1554 (1911).

that the adsorption from moderately concentrated solutions may be regarded as almost irreversible. It is, therefore, strong negative adsorption by the adsorption complex which prevents the passage of both sugar and ferrocyanide ion through the membrane. As ordinarily prepared, one side at least of a copper ferrocyanide membrane is practically saturated with potassium ferrocyanide so that the positive adsorption is negligible from dilute solutions of the salt. The permeability of the membrane to relatively high concentrations of ferrocyanide ion is due to two facts: (1) the adsorption of ferrocyanide ion is not completely irreversible from strong solutions of potassium ferrocyanide and (2) the colloidal film is partially coagulated by the salt, opening up cracks at weak points in the membrane. The permeability of the membrane for a series of ions is in the order: chloride > sulfate > ferrocyanide, which is the reverse of the order of adsorption by the gel.

In the third case, the parchment functions as a typical dialyzing membrane, the concentration, osmotic, and electrical effects being due to the inability of the large Congo red ion or ionic micelle of the so-called colloidal electrolyte to diffuse through the pores.

As Donnan¹ has emphasized, the theory of membrane equilibria depends on but two assumptions: the existence of equilibrium and the existence of certain restraints which restrict the free diffusion of one or more of the ionized constituents. This theory has been used successfully by Procter and Wilson² and Loeb³ to calculate the swelling of acids, such as gelatin in hydrochloric acid, on the assumption that gelatin is an elastic jelly insoluble in, but permeable to, water which forms a definite highly ionized salt, gelatin hydrochloride, in accord with the following equation:



Now, the GH^+ ion, being a part of the elastic jelly, cannot diffuse. This constraint results in a Donnan equilibrium by imposing a restraint on the equal distribution of ions within and without

¹ *Chem. Reviews*, **1**, 87 (1924).

² PROCTER: *J. Chem. Soc.*, **105**, 313 (1914); *Kolloidchem. Beihefte*, **2**, 243 (1911); PROCTER and WILSON: *J. Chem. Soc.*, **109**, 307 (1916); WILSON and WILSON: *J. Am. Chem. Soc.*, **40**, 886 (1918).

³ "Proteins and the Theory of Colloidal Behavior" (1922).

the jelly. By applying the Donnan equilibrium and Hooke's law, values were calculated for the swelling of gelatin in different concentrations of acid, in good agreement with the observed values. This agreement was believed to furnish conclusive proof that gelatin and hydrochloric acid interact to form a definite salt, gelatin hydrochloride. In reaching this conclusion, the important fact has been overlooked that prediction of results by means of a formula does not furnish conclusive proof of the assumption on which the formula is based. In the case under consideration, one can get exactly the same constraint, namely, inability of a charged particle to diffuse freely, and therefore exactly the same formulas and make exactly the same predictions by making the more probable assumption that hydrogen ion is preferentially adsorbed on the surface of gelatin particles rather than entering into definite chemical combination with the particles.¹

¹ Cf. WEISER: "The Hydrous Oxides," 21 (1926).

CHAPTER XVIII

IONIC ANTAGONISM IN COLLOID SYSTEMS

The antagonistic action of ions was first pointed out by Ringer¹ who recognized the profound importance of suitable mixtures of electrolytes in promoting the life and growth of cells. Since biologists frequently compare the wall of the living cell to a membrane of copper ferrocyanide, and since certain salt pairs act antagonistically on the stability of copper ferrocyanide sols, it seems fitting to discuss the general subject of ionic antagonism in colloid systems in connection with the colloidal ferrocyanides.

IONIC ANTAGONISM IN THE NEUTRALIZATION OF SOLS BY SINGLE ELECTROLYTES

In the precipitation by electrolytes of sols stabilized by preferential adsorption of ions, it is usually considered that only anions count in the case of positive sols and only cations count in the case of negative sols. In earlier chapters it has been emphasized that the influence of the ions having the same charge as the sol, the stabilizing ion, cannot be disregarded entirely in any case, and may be quite marked if the electrolyte precipitates only in high concentration. The precipitation value of electrolytes for sols should be defined, therefore, as that concentration which results in sufficient adsorption of the precipitating ion to neutralize below a critical value the combined adsorption of the original stabilizing ion and the stabilizing ion added with the precipitating solution. There is, thus, an antagonistic action between the oppositely charged ions of a precipitating electrolyte in the sense that the greater the adsorption of the stabilizing ion the greater must be the adsorption of the precipitating ion to reduce the charge below the critical value. Hence, the precipitation value of an electrolyte with a strongly adsorbed stabilizing ion is necessarily higher than that of an electrolyte with a weakly

¹ *J. Physiol.* **3**, 380 (1880-82); **4**, 29, 222 (1882-83); **7**, 118, 291 (1886).

adsorbed stabilizing ion. This is illustrated by the data summarized in Table XLII.

TABLE XLII.—ANTAGONISTIC ACTION BETWEEN OPPositELY CHARGED IONS IN THE NEUTRALIZATION OF SOLS

Negative sols		Arsenic trisulfide	Copper ferrocyanide
Precipitation values of potassium salts	Chloride	33.2	35.6
	Sulfate	43.5	47.5
	Ferrocyanide	71.2	260.0
Positive sols		Ferric oxide	Chromic oxide
Precipitation values of chlorides	Potassium	9.0	30.0
	Barium	9.65	31.8
	Hydrogen	400.0	

Just as the precipitating power of an electrolyte decreases with increasing adsorbability of the antagonistic stabilizing ion, so the precipitating power of electrolytes with the same stabilizing ion increases with increasing adsorbability of the precipitating ion. This is illustrated in Table XLIII¹ which gives the precipitation value of barium chloride and of various alkali chlorides for arsenic trisulfide, together with the adsorption of barium

TABLE XLIII

Electrolyte added to 100 cubic centimeters sol, total volume, 200 cubic centimeters	Barium adsorbed		Precipitation value, milliequivalents per liter	
	Gram	Milliequivalent per gram	BaCl ₂	
30 cubic centimeters N/50 BaCl ₂	0.0109	0.058	BaCl ₂	2.74
30 cubic centimeters N/50 BaCl ₂ + 30 cubic centimeters N/2 LiCl....	0.0037	0.019	LiCl	88.7
30 cubic centimeters N/50 BaCl ₂ + 30 cubic centimeters N/2 NaCl....	0.0025	0.014	NaCl	73.5
30 cubic centimeters N/50 BaCl ₂ + 30 cubic centimeters N/2 KCl....	0.0018	0.009	KCl	63.7
30 cubic centimeters N/50 BaCl ₂ + 30 cubic centimeters N/2 HCl....	0.0013	0.007	HCl	52.5

¹ WEISER: *J. Phys. Chem.*, **29**, 955 (1925).

during the precipitation of the sol with barium chloride alone and when mixed with constant amount of the several alkali chlorides. From the observations it will be noted that univalent ions cut down the adsorption of barium in the order: lithium < sodium < potassium < hydrogen. Since, under otherwise constant conditions, one should expect the adsorption of a given cation to be cut down by the presence of a second cation in proportion to the adsorbability of the latter, it follows that the order of adsorbability of the univalent ions is: hydrogen > potassium > sodium > lithium. This is exactly the same as the order deduced from the precipitation values of the salts, assuming that the salt containing the most readily adsorbed cation precipitates in lowest concentration.

It should be pointed out in passing that the results recorded in Table XLIII furnish almost conclusive proof that the univalent cations are adsorbed less strongly¹ than bivalent barium. For example, the adsorption of barium is cut down but very little by the presence of an equivalent amount of lithium; and twenty-five times the concentration of lithium cuts it down but two-thirds of the value in the absence of lithium.

ONIC ANTAGONISM IN THE NEUTRALIZATION OF SOLS BY MIXTURES

Thirty years ago Linder and Pieton² observed that the precipitating action of mixtures of two electrolytes for arsenic trisulfide sol is approximately additive provided the precipitating power of each is of the same order of magnitude, whereas the precipitating action may rise appreciably above an additive relationship if the electrolytes vary widely in their precipitating power. Thus the precipitating action of mixtures of SrCl_2 and BaCl_2 are nearly additive, whereas the addition of potassium chloride increases rather than decreases the precipitation concentration of strontium chloride. This cannot be attributed to a decrease in the dissociation of strontium chloride by potassium chloride because other potassium salts, such as the nitrate, give similar results. Since this so-called ionic antagonism was not observed with gold sol

¹Cf., however, DHAR, SEN and GHOSH: *J. Phys. Chem.*, **28**, 457 (1924).

²*J. Chem. Soc.*, **67**, 67 (1895).

and with von Weimarn's¹ sulfur sol, but was observed with Odén's² sulfur sol which is hydrous, Freundlich and Scholz³ conclude that the hydration of the sol and of the precipitating ion are of primary importance in producing ionic antagonism and so in determining whether the precipitating action of mixtures shall be additive or above the additive value. This leads to the deduction that arsenic trisulfide sol is a hydrophile sol although it is not usually so considered; and to the suggestion that the behavior of colloids with mixtures is a suitable means of determining to what extent the stability is influenced by hydration. The general accuracy of these conclusions is rendered questionable by some observations on the precipitation of chromic oxide sol⁴ by mixtures of electrolytes having widely different precipitating power, such as potassium chloride and potassium sulfate. Although the sol is very highly hydrous the precipitation values of mixtures are less than additive by a quite appreciable amount instead of being considerably above the additive values as the theory of Freundlich and Scholz would predict. One may be quite certain, therefore, that hydration is not the only factor in bringing about the phenomenon of ionic antagonism and may be a relatively unimportant one in certain cases.

As a result of an investigation of this anomalous behavior, in 1921,⁵ it was concluded that, in the simultaneous adsorption by solids from mixtures of two electrolytes having no ion in common, the most readily adsorbed cation and anion are taken up most and the other pair least readily; while from mixtures having one ion in common, the oppositely charged ions are each adsorbed less than if the other were absent but the most readily adsorbed ion is displaced the least. From this, there would appear to be two factors which influence the precipitating action of mixtures of electrolytes: (1) the antagonistic effect of each precipitating ion on the adsorption of the other and (2) the stabilizing influence of the ions having the same charge as the sol.

¹ VON WEIMARN and MALYSCHEW: *Kolloid-Z.*, **8**, 216 (1911).

² "Der kolloide Schwefel" (1913).

³ *Kolloidchem. Beihefte*, **16**, 267 (1922); cf., also, NEUSCHLOSZ: *Pfluger's Arch.*, **181**, 17 (1920).

⁴ WEISER: *J. Phys. Chem.*, **28**, 232 (1924).

⁵ WEISER: *J. Phys. Chem.*, **25**, 665 (1921).

As an illustration of the antagonistic action of salts of varying precipitating power, the observations with mixtures of LiCl and BaCl₂ on arsenic trisulfide sol are given in Table XLIV.¹ It will be seen that the presence of alkali chloride increases appreciably the precipitation concentration of barium chloride. In Table XLV is given the effect of the presence of lithium on the adsorption of barium during the precipitation of arsenic trisulfide sol. Experiment 1 gives the adsorption of Ba⁺⁺ ion at the precipitation

TABLE XLIV.—PRECIPITATION OF COLLOIDAL AS₂S₃ WITH MIXTURES OF LiCl AND BaCl₂

N/2 LiCl taken, cubic centimeters	N/100 BaCl ₂ to complete coagulation			Difference	
	Taken, cubic centimeters	Calculated, cubic centimeters			
			Cubic centimeters	Per cent	
4.05					
....	4.03				
0.5	4.50	3.54	0.96	27	
1.0	4.25	3.03	1.22	38	
2.0	3.76	2.03	1.73	84	
3.0	2.25	1.03	1.22	118	

concentration of BaCl₂; experiments 2, 3, and 4 give (a) the adsorption of Ba⁺⁺ ion from BaCl₂ alone at the concentration necessary to cause precipitation from the mixture with LiCl, and (b) the adsorption of Ba⁺⁺ ion in the presence of Li⁺ ion. Attention should be called to the fact that the concentration of LiCl and BaCl₂ used in experiments 2, 3, and 4 correspond to those for 0.5, 1.0, and 2.0 cubic centimeters of LiCl, respectively, in Table XLIV.

From these observations it is obvious that concentrations of lithium below the precipitation value have a marked influence on the adsorption of barium. Thus, at the precipitation concentrations of a mixture containing one-eighth the precipitation value

¹ WEISER: *J. Phys. Chem.*, **28**, 232 (1924); cf., also, BOUTARIC and PERREAU: *Compt. rend.*, **180**, 1337 (1925); BOUTARIC and MANIÈRE: *Ibid.*, **180**, 1841 (1925).

of LiCl alone, the adsorption of Ba⁺⁺ ion is lowered more than 25 per cent; while from a mixture containing one-half the precipitation value of LiCl alone, the adsorption of Ba⁺⁺ ion is decreased 53 per cent. At the same time the presence of Ba⁺⁺ ion unquestionably influences the adsorption of Li⁺ ion so that the concentra-

TABLE XLV.—ADSORPTION BY ARSENIC TRISULFIDE OF BARIUM IN THE PRESENCE OF LITHIUM

N/2 LiCl	N/100 BaCl ₂	H ₂ O		Average	Barium adsorbed	
					Grams	Grams per mol As ₂ S ₃
0	50.80	74.20	0.0288	0.0284	0.0140	1.214
0	50.80	74.20	0.0280			
0	56.25	68.75	0.0316	0.0319	0.0151	1.310
0	56.25	68.75	0.0322			
6.25	56.25	62.50	0.0371	0.0373	0.0112	0.971
6.25	56.25	62.50	0.0375			
0	53.10	71.90	0.0304	0.0302	0.0143	1.250
0	53.10	71.90	0.0301			
12.50	53.10	59.40	0.0363	0.0365	0.0097	0.841
12.50	53.10	59.40	0.0368			
0	47.00 ¹	73.00	0.0259	0.0260	0.0132	1.145
0	47.00	73.00	0.0260			
25.00	47.00 ¹	48.00	0.0358	0.0357	0.0600	0.520
25.00	47.00	48.00	0.0355			

¹ +5 cubic centimeters MgCl₂.

tion necessary for sufficient adsorption to decrease the charge on the particles below the critical value is proportionately greater for each salt in the presence of the other. This mutual ionic antagonism would appear to be an important factor in raising the precipitation concentration of certain mixtures above the additive value.

Associated with the cationic antagonism is the antagonistic action of chloride, the adsorption of which cannot be ignored at the relatively high concentration of LiCl employed. In most cases, Dhar and his collaborators¹ rule out the influence of cationic antagonism in increasing the precipitation value of certain salt pairs above the additive value, and attribute the effect entirely to the stabilizing action of the anions, chloride ion in the case at hand. Some further observations bear on this point:

In Table XLIII, it was pointed out that the same concentration of different alkali chlorides cuts down the adsorption of barium ion to widely different degrees. It seemed probable, therefore, that the precipitation value of barium chloride would vary in the presence of approximately the same concentration of chloride

TABLE XLVI.—PRECIPITATION OF As_2S_3 WITH MIXTURES
(Precipitation values in milliequivalent per liter)

<i>a</i>		<i>b</i>		<i>c</i>	
LiCl	BaCl ₂	NaCl	BaCl ₂	KCl	BaCl ₂
0.0	1.60	0.0	1.60	0.0	1.60
12.5	2.02	12.5	1.93	12.5	1.88
25.0	2.18	25.0	1.98	25.0	1.92
43.7	2.13	43.7	1.82	43.7	1.62
62.5	1.78	62.5	1.30	62.5	1.05
81.2	1.23	95.0	0.00	83.0	0.00
111.2	0.00				
<i>d</i>		<i>e</i>		<i>f</i>	
HCl	BaCl ₂	KCl	NaCl	KCl	CeCl ₃
0.0	1.60	0.0	95.0	0.0	0.388
12.5	1.98	25.0	64.0	12.5	0.230
25.0	1.93	50.0	35.0	25.0	0.162
37.5	1.65	83.0	0.0	37.5	0.132
50.0	1.00	50.0	0.105
61.5	0.00	62.5	0.067
				83.0	0.000

¹ *J. Phys. Chem.*, **28**, 313, 457, 1029 (1924); **29**, 435, 517, 659 (1925); *Kolloid-Z.*, **34**, 262 (1924); **36**, 129 (1925); *Z. anorg. Chem.*, **142**, 345 (1925); See, also, MUKHERJEE and GHOSH: *Quart. J. Indian Chem. Soc.*, **1**, 213 (1924).

ion but with different alkali cations. That such is the case is shown clearly by observations recorded in *a*, *b*, *c*, and *d*, Table XLVI, and shown graphically in Fig. 27.¹

It will be noted that the precipitation value of barium chloride is increased by like amounts of alkali chlorides in the order: $\text{LiCl} > \text{NaCl} > \text{KCl}$; while in the presence of HCl, the precipitation value of barium salt first rises to a point just below that in the presence of a like amount of lithium chloride and then drops

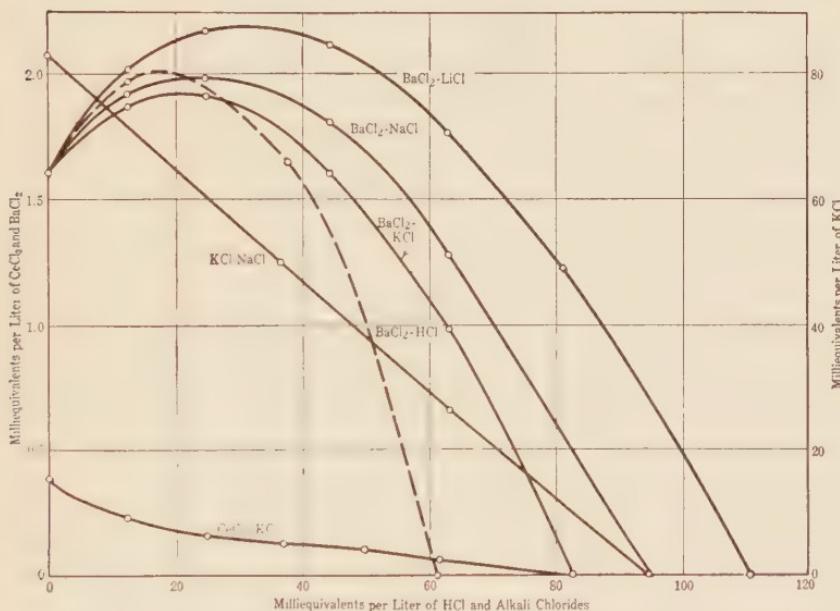


FIG. 27.—Coagulation of arsenic trisulfide sol by mixtures of electrolytes.

off rather sharply. Since the adsorbability of the alkalies is in the order $K > Na > Li$, it may be reasoned that the stabilizing action of chloride ion will be greater in the presence of lithium ion than of potassium ion, thus accounting for the higher precipitation values of barium chloride in the presence of lithium chloride than of potassium chloride. This would not account for the behavior of mixtures of hydrochloric acid and barium chloride, for, at certain concentrations of chloride, the precipitation value in the presence of the relatively strongly adsorbed hydrogen ion is

¹ WEISER: *J. Phys. Chem.*, **30**, 20 (1926).

similar to that in the presence of lithium ion and greater than that in the presence of either sodium or potassium ion.

Another explanation suggests itself: For a given alkali chloride concentration, precipitation will take place when the combined adsorption of the two cations neutralizes the combined adsorption of chloride and hydrosulfide ions. The combined adsorption will be equivalent for different pairs of cations; but the relative amounts of each that make up this equivalent adsorption will vary, depending, as it does, on the relative adsorbability of the two cations. If one may disregard for the moment the slight variation in the amounts of chloride added with barium chloride as compared with the relatively large amount of this ion added with the alkali chloride, it follows that, for a given concentration of different alkali chlorides, the varying amounts of barium that must be added will depend on the effect of each cation on the adsorption of the other. Thus the adsorption of barium is cut down by lithium ion less than by potassium ion, tending to make the precipitation concentration of barium chloride less in the presence of lithium chloride than of potassium chloride. Hand in hand with this is the decrease by barium of the adsorption of alkali which will tend to make the precipitation concentration of barium chloride higher in the presence of lithium. From this point of view, the latter factor appears to predominate with the alkali chlorides. With hydrochloric acid, however, the cutting down of the adsorption of barium by hydrogen ion is the determining factor with lower concentration of hydrochloric acid while with higher concentration of acid, the second factor appears to predominate.

Another method of attack is to determine whether the presence of a relatively small amount of potassium chloride, say, increases the precipitation value for arsenic trisulfide sol, of chlorides other than barium chloride. From the results recorded in *e* and *f*, Table XLVI, and shown graphically in Fig. 27, it is clear that the addition of potassium chloride does not increase the stability of arsenic trisulfide sol toward all other chlorides. Thus the relationship is approximately additive with sodium chloride, whereas the precipitation value of cerium chloride is decreased unmistakably by the presence of potassium chloride. It hardly seems probable that the latter result would obtain if potassium

chloride in small concentration actually stabilized the sol in the same way that a highly purified ferric oxide sol is stabilized by the addition of a small amount of hydrogen ion or ferrocyanide sols by a small amount of ferrocyanide. In the absence of marked ionic antagonism between ions of the same sign, one might expect the precipitation values of mixtures to fall below the additive value on account of the relatively greater adsorbatibility of the precipitating ions at low concentration. This was actually observed in a number of instances with hydrous oxide sols.¹ To account for the difference in the results with barium chloride and cerium chloride, one should expect to find the adsorption of barium cut down much more strongly than cerium by the presence of proportionate amounts of potassium chloride. That such is the case is shown by the results recorded in Table XLVII on the adsorption of barium and of cerium, respectively, in the

TABLE XLVII

EFFECT OF POTASSIUM ION ON THE ADSORPTION OF BARIUM ION AND CERIUM ION

Solutions mixed with 100 cubic centimeters sol. Total volume, 200 cubic centimeters		$N/200 \text{ CeCl}_3$ remaining, cubic centimeters	Ce adsorbed, milliequivalent per gram
$N/200 \text{ CeCl}_3$	$N/2 \text{ KCl}$		
20	0	5.4	0.073
20	5	9.0	0.058
$N/50 \text{ BaCl}_2$	$N/2 \text{ KCl}$	BaSO_4 remaining in 180 cubic centimeters	Ba adsorbed, milli-equivalent per gram
30	0	0.0537	0.064
30	30	0.0615	0.010

presence of fifty times the concentration of potassium chloride. It will be noted that, under similar conditions, the adsorption of cerium is cut down less than 25 per cent, while the adsorption of barium is cut down almost 85 per cent.

Finally, the presence of potassium chloride does not raise the precipitation concentration of sodium chloride above the additive value as would be expected if the sol were stabilized appreciably by preferential adsorption of chloride ion. The precipitation value, of such mixtures having a common anion are additive

¹ WEISER: *J. Phys. Chem.*, **28**, 232 (1924).

since the adsorptions of the precipitating cations are similar and so the adsorption of each is affected but slightly by the presence of the other within the limits of the precipitation concentration. On the other hand, with mixtures having precipitating cations in common and different anions, one should expect variations

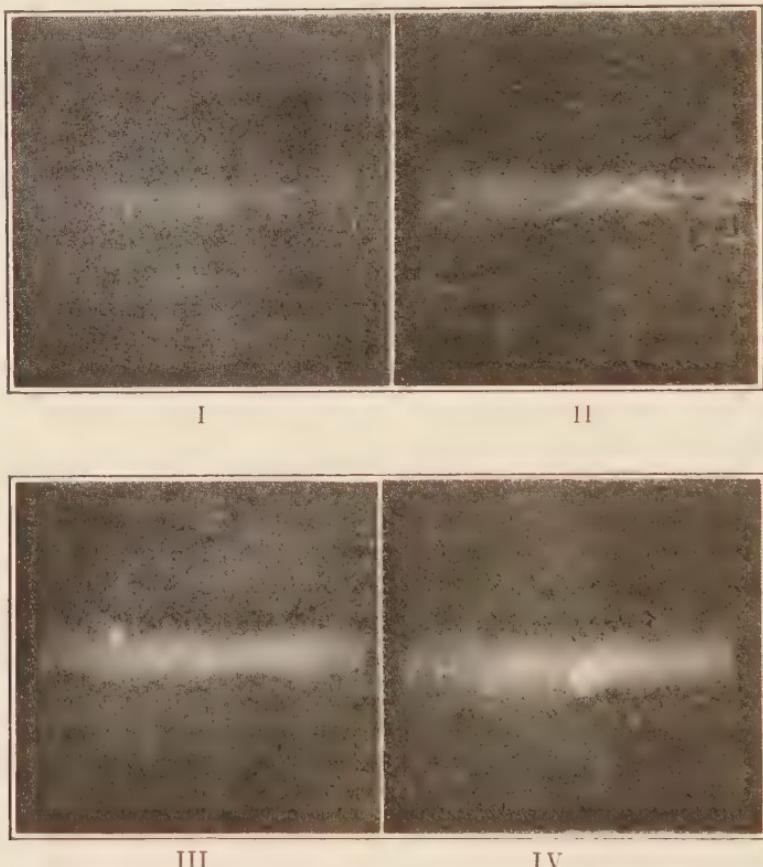


FIG. 28.—Photographs of light cones in the ultramicroscope of an arsenic trisulfide sol (I) without sodium chloride (II, III, and IV) with 10, 25, and 50 milliequivalents of sodium chloride per liter, respectively.

from additive values in proportion to the difference in adsorbability of the anions. Thus, the precipitation concentrations for mixtures of potassium and sodium ferrocyanide were found to be additive whereas the critical concentrations for mixtures of potassium chloride and ferrocyanide rise slightly above the

additive values¹ because of the greater adsorbability of ferrocyanide ion than of chloride ion.

That the stabilizing action of adsorbed chloride ion may not be the most important factor in increasing the precipitation value of mixtures above the additive relationship is further indicated by the agglomerating action of relatively low concentrations of alkali chloride. An arsenic trisulfide sol was prepared according to the method of Freundlich and Nathansohn.² This sol, when viewed in the ultramicroscope, gives a light cone but is practically free from ultramicrons. The addition of small amounts of NaCl causes some agglomeration of the particles, as evidenced by the appearance of ultramicrons on standing. This phenomenon was investigated carefully in the following way: A quantity of the sol was prepared and filtered through an ultrafilter which removed any ultramicrons that might be present. The preparation gave a clear uniform light cone. Samples of 10 cubic centimeters each of the sol were taken and diluted to 20 cubic centimeters with ultrafiltered water to which was added 0, 0.2, 0.5, and 0.7 cubic centimeter respectively, of ultrafiltered normal sodium chloride. Special care was taken in the cleaning of all apparatus with ultrafiltered water and in protecting the samples from dust. After standing for 2 hours, the samples were placed in the Biltz cell of a Zeiss slit ultramicroscope supplied with a camera, and the light cone photographed. The time of exposure was 2 minutes. A comparison of the photographs obtained (Fig. 28) indicates agglomeration of particles in the presence of relatively small amounts of sodium chloride, as evidenced by the gradually increasing intensity of the light cone in going from sample 1 containing no sodium chloride to sample 4 containing 0.7 cubic centimeter of the normal salt.

For the sake of comparison, the precipitation value curve of mixtures of barium chloride and sodium chloride for the sol is given in Fig. 29. The ultramicroscopic observations referred to above were made on the pure sol and on samples containing 10, 25, and 35 milliequivalents of sodium chloride per liter, respectively. In this region the precipitation value of barium chloride is increased appreciably by the presence of sodium

¹ Cf. SEN: *J. Phys. Chem.*, **29**, 517 (1925).

² *Kolloid-Z.*, **28**, 258 (1921).

chloride although the agglomeration of the particles by the latter is clearly indicative of a decrease in the stability of the sol. It would seem, therefore, that in this case, cationic antagonism rather than the stabilizing action of the anion is the important factor in bringing about the variation from an additive relationship.

Ionic antagonism such as that between alkali and alkaline earth cations in the precipitation of arsenic trisulfide sol has been

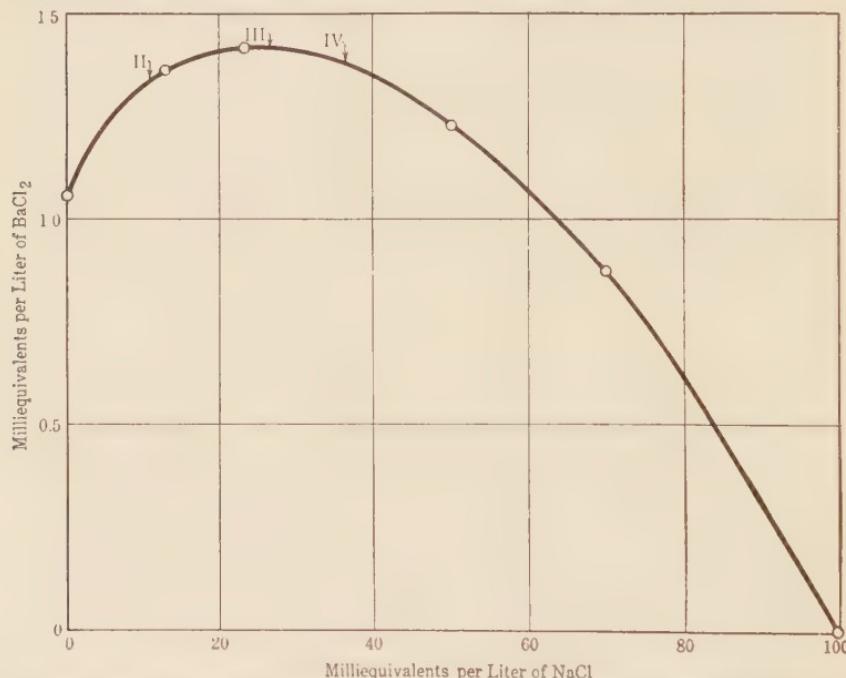


FIG. 29.—Coagulation of arsenic trisulfide sol by mixtures of sodium chloride and barium chloride.

recognized recently by other investigators. Thus, Mann¹ finds that NH_4Cl , MgCl_2 , and AlCl_3 cut down the adsorption of methylene blue and neutral red by discs of mangold root, the magnitude of the reduction being a function of the valency and concentration of the cation. The adsorption of both dye and salt attain equilibrium at a lower point than would be reached by either in the absence of the other, indicating mutual hindrance. As already pointed out, Dhar and his collaborators have ignored

¹ *Ann. Bot.*, **38**, 753 (1924).

or opposed the concept of antagonism between ions of the same charge but they are not consistent and it is difficult to know what position they will take in a given case. For example, in a recent paper¹ they say:

As is known, crystal violet and strychnine hydrochloride cations are more strongly adsorbed by arsenic trisulfide than barium and aluminum ions. On this account, the presence of the dye cations cuts down the adsorption of K⁺, Ba⁺⁺ and Al⁺⁺⁺ ions and therefore more than the calculated amount of KCl, BaCl₂, and Al(NO₃)₃ is required for the precipitation of the sol. On the other hand, in precipitating arsenic trisulfide sol with mixtures of strychnine chloride and crystal violet, the values are practically additive since the cations of both substances are about equally adsorbed and, at the precipitation concentration, there is no antagonistic effect on the adsorption.

Although, in certain cases, the antagonistic action between precipitating ions may be an important factor in determining the precipitation values of salt pairs; in other instances the effect of stabilizing ions may predominate. Thus, Sen² working with copper ferrocyanide sol, observed an increase in precipitation value of potassium chloride and of barium chloride in the presence of potassium ferrocyanide. With mixtures of potassium chloride and potassium ferrocyanide, it is quite obvious that cationic antagonism cannot come in, since both precipitating cations are the same. Mukherjee and Ghosh³ observed a similar behavior with mixtures of sodium benzoate and sodium chloride on arsenic trisulfide sol and the author has already called attention to observations with potassium ferrocyanide and potassium chloride on the same sol. The determining factor in the latter cases is the stabilizing action of the relatively strongly adsorbed benzoate and ferrocyanide, respectively.

Consider the case of Graham's ferric oxide sol, which owes its stability to preferential adsorption of hydrogen ion derived from hydrolysis of ferric chloride. It is too well known to need comment, that the stability of the sol falls off as the hydrogen ion concentration is decreased by dialysis and if the dialysis is continued long enough, all of the sol will precipitate. Conversely,

¹ GHOSH, BHATTACHARYA, and DHAR: *Kolloid-Z.*, **38**, 145 (1926).

² *J. Phys. Chem.* **29**, 534 (1925).

³ *Quart. J. Indian Chem. Soc.*, **1**, 213 (1924).

if we add hydrochloric acid to a highly purified sol, the stability toward all electrolytes will increase. Similar stabilization would be expected on adding ferric chloride, aluminum chloride, or lanthanum nitrate, as Freundlich and Wosnessensky¹ have shown. With the relatively insoluble Péan de St. Gilles sol, a maximum in the stability is reached on adding hydrochloric acid; and at a suitable concentration, the adsorption of the precipitating chloride ion neutralizes the adsorption of hydrogen ion and precipitation takes place.² Similarly, colloidal copper ferrocyanide and Prussian blue are stabilized by preferential adsorption of ferrocyanide ion. The lower the concentration of the ferrocyanide ion the less the stability. On adding potassium ferrocyanide to a highly purified ferrocyanide sol, the stability toward all electrolytes should be increased until the concentration is high enough for the adsorption of the precipitating potassium ion to decrease the stability of the sol below the critical value. This is exactly what Sen observed with two electrolytes of widely varying precipitating power. The precipitation value of both potassium chloride and barium chloride is increased to a maximum that lies above the value for either electrolyte alone.³

A survey of the data obtained by Sen indicates that the form of the precipitation value curve of salt pairs for negative colloidal copper ferrocyanide sol depends on whether cationic antagonism may come in or whether it is eliminated by using salt pairs with a common cation. Thus when precipitation concentration of potassium ferrocyanide as abscissa is plotted against that of potassium chloride as ordinate, the curve rises sharply to a maximum, bends sharply, and then follows an almost straight course to the precipitation value of pure potassium ferrocyanide. On the other hand, with concentrations of barium chloride as ordinate, the curve rises gradually to a broad maximum, dropping sharply when near the precipitation value of pure potassium ferrocyanide. The difference between these curves obtained with the ferrocyanide sol, and between either of them and curves obtained with arsenic trisulfide sol called for further

¹ *Kolloid-Z.*, **33**, 222 (1923).

² WEISER: *J. Phys. Chem.*, **25**, 665 (1921).

³ SEN: *J. Phys. Chem.*, **29**, 517, 539 (1925); SEN and MEHROTRA: *Z. anorg. Chem.*, **142**, 345 (1925).

investigation. Accordingly, a highly purified copper ferrocyanide sol was prepared and the precipitation concentration of salt pairs was determined taking special precautions to obtain accurate values. The results with mixtures of potassium ferrocyanide and both potassium chloride and barium chloride are given in Table XLVIII and shown graphically in Fig. 30.¹

TABLE XLVIII.—PRECIPITATION OF COLLOIDAL $\text{Cu}_2\text{Fe}(\text{CN})_6$ BY MIXTURES
(Precipitation values in milliequivalents per liter)

$\text{K}_4\text{Fe}(\text{CN})_6$	BaCl_2	$\text{K}_4\text{Fe}(\text{CN})_6$	KCl
0.0	1.58	0.0	23.8
12.5	1.90	12.5	157.5
25.0	2.00	25.0	155.0
50.0	2.10	50.0	140.0
100.0	2.00	100.0	112.5
150.0	1.60	150.0	82.5
262.5	0.00	262.5	0.0

It will be seen that the addition of potassium ferrocyanide causes the precipitation value of potassium chloride to mount sharply to a value more than six times that of pure chloride. This indicates that the purity of the original sol with respect to ferrocyanide ion is quite high. After the maximum is reached, the curve bends sharply and then follows an almost linear course, as Sen also observed. This means that if one takes an impure copper ferrocyanide sol, the precipitation values of mixtures of potassium ferrocyanide and chloride will be approximately additive on account of the absence of cationic antagonism. A similar type of curve should result with mixtures of barium ferrocyanide and barium chloride. This was found to be true so far as the linear part of the curve is concerned; but the sharp maximum could not be detected with certainty since the precipitation concentrations of the chloride and ferrocyanide of barium were so close together.

On turning to the potassium ferrocyanide-barium chloride curve, contrary to Sen's observations, one is impressed with the very great similarity to the curves obtained with alkali-alkaline earth salt pairs on arsenic trisulfide sol. Since in the latter

¹ WEISER: *J. Phys. Chem.*, **30**, 1531 (1926).

case both cationic antagonism and the stabilizing action of the anion play a role, it is possible that the difference between the potassium ferrocyanide-barium chloride curve and the potassium ferrocyanide-potassium chloride curve with copper ferrocyanide sol, is due to the absence of cationic antagonism in the first instance and its presence in the second.

It should be emphasized, however, that the initial increase in precipitation value of BaCl_2 in the presence of potassium ferro-

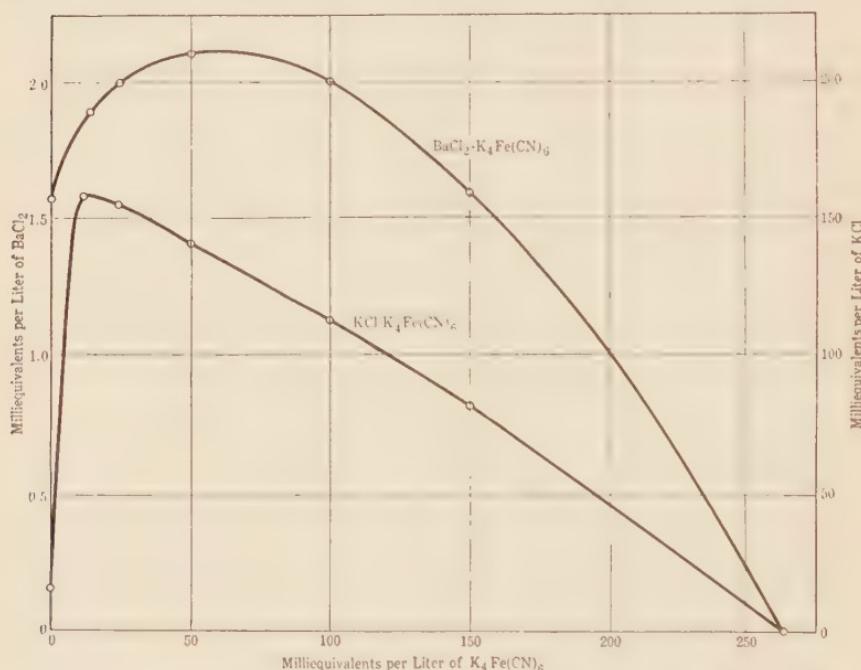


FIG. 30.—Coagulation of copper ferrocyanide by mixtures of electrolytes.

cyanide is due primarily to the effect of ferrocyanide ion. Thus, the precipitation values of mixtures of potassium chloride and barium chloride fall slightly below the additive value at the lower concentrations of potassium chloride, but at higher concentrations of potassium chloride the values are slightly greater than additive. The same is true for mixtures of potassium chloride and cupric chloride and of potassium chloride and cupric sulfate.¹ For

¹ Cf., however, GURCHOT: *J. Phys. Chem.*, **30**, 98 (1926).

arsenic trisulfide sol the antagonism between potassium and barium ferrocyanide is greater than between the corresponding chlorides and a similar condition doubtless exists with copper ferrocyanide sols.

As a result of these observations, it is evident that the precipitation values for sols of mixtures of two electrolytes may be additive, may be greater than the additive values, or may be less than the additive values. Moreover, it would seem that three factors, at least, may influence the precipitation concentration of salt pairs: (1) The effect of each precipitating ion on the adsorption of the other, (2) the stabilizing action of ions having the same charge as the sol, and (3) the relatively greater adsorbability of ions at lower concentrations. The antagonistic action between precipitating ions of the same charge is important in raising the critical concentrations above the additive value only in case the ions show marked differences in adsorbability. Variation from the additive relationship with mixtures of salt pairs having a common precipitating ion results only when there is an appreciable difference in the adsorbability of the stabilizing ions, the magnitude of the variation from an additive relationship being determined by the differences in adsorbability. If the first and second factors referred to above are not too pronounced, the precipitation values of mixtures may fall below the additive value on account of the relatively greater adsorbability of precipitating ions at low concentration.

Since the addition of alkali chloride to arsenic trisulfide sol and of alkali ferrocyanide to copper ferrocyanide sol increases the precipitation value of BaCl_2 , the question arises whether the sols coagulated by BaCl_2 alone will be repeptized by the addition of alkali salt. The answer is that it will be provided the alkali salt exerts an appreciable peptizing action. When a sol like Freundlich and Nathansohn's arsenic trisulfide is treated with barium chloride the very minute primary colloidal particles coalesce into larger primary ultramicros which finally agglomerate into secondary particles and these, in turn, into clumps. If potassium chloride is added to such a coagulum, a sol is not reformed on account of the relatively low peptizing action of chloride ion. On the other hand, the addition of potassium ferrocyanide to a copper ferrocyanide coagulum reverses the coagulation on

account of the marked peptizing action of the anion on copper ferrocyanide gel.

Mixtures of certain electrolytes act antagonistically on a lecithin sol, as shown by Neuschlosz.¹ Instead of determining precipitation concentrations, he followed the effect of electrolytes on surface tension change which is unquestionably connected with coagulation. Because of the hydrophilic nature of the negatively charged sol, the method probably serves to detect

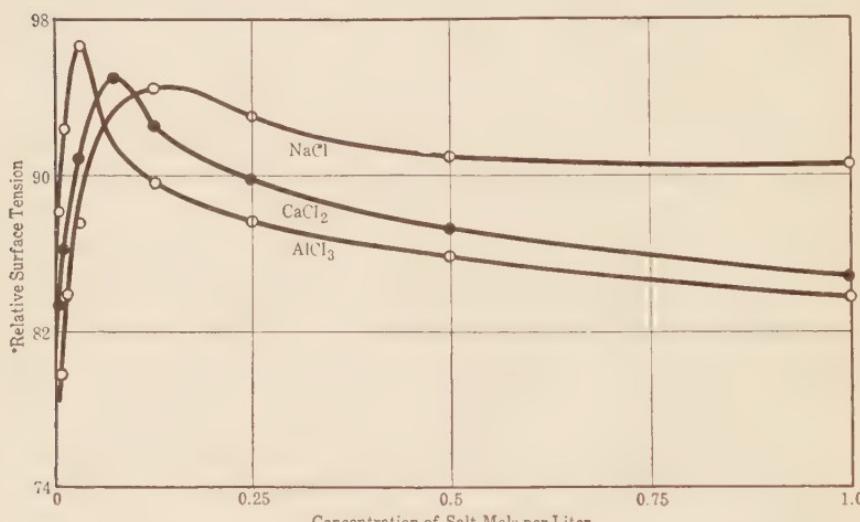


FIG. 31.—Surface tension of lecithin sol in solutions of single electrolytes.

smaller changes than a method based on visible flocculation. In Fig. 31 is given the effect of varying concentrations of the chlorides of sodium, calcium, and aluminum on the relative surface tension as determined by the stalagmometer. The pure 1 per cent lecithin sol has a smaller surface tension than pure water. Upon adding gradually increasing amounts of electrolyte, the surface tension first increases to a maximum and then decreases. Neuschlosz attributes the initial increase to coagulation of the lecithin particles to coarser aggregates which diminish the surface tension less than the finer particles of the pure sol. This is strongly indicated by the fact that the maximum is reached at

¹ *Pfluger's Archiv.*, **181**, 17 (1920); **187**, 136 (1921); *Kolloid-Z.*, **27**, 292 (1920).

a higher concentration for univalent sodium ion than for bivalent calcium ion and for the latter at a higher concentration than for trivalent aluminum ion, in accord with Schulze's rule. The decrease in surface tension at the higher concentrations of electrolytes is attributed to repeptization of the particles as a positive sol. In line with this, the right-hand portion of the curve for aluminum chloride which gives the strongly adsorbed aluminum ion lies below the calcium chloride curve and the latter in turn below the sodium chloride curve.

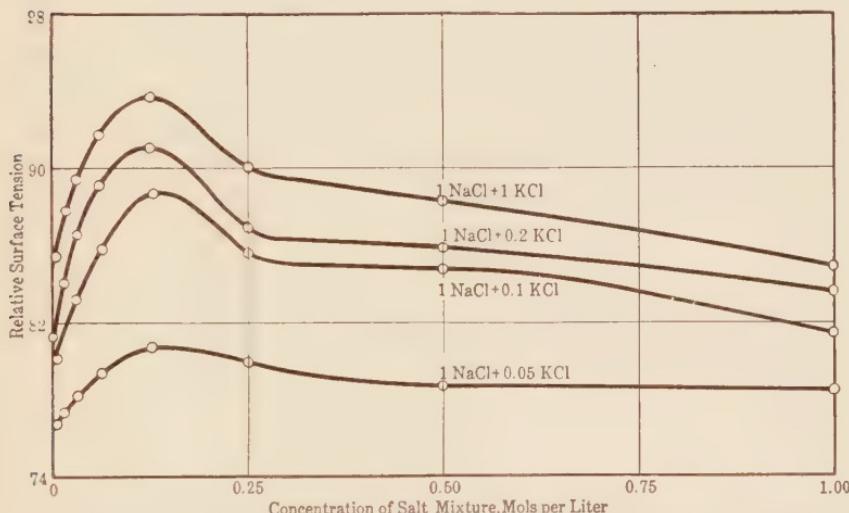


FIG. 32.—Surface tension of lecithin sol in solutions of mixtures of electrolytes.

Suitable mixtures of electrolytes having a common anion and different cations produce a negligible change in the surface tension, in contrast to the effect of single electrolytes. This is illustrated for mixtures of sodium and calcium chloride, as shown in Fig. 32. In this case the relative surface tensions for mixtures of $1\text{ NaCl} + \frac{1}{2}0\text{ CaCl}_2$ remain almost constant throughout the entire range of concentration between $\frac{1}{3}2$ molar and molar, the value being approximately that of the salt-free sol, 75.9. A smaller or larger relative content of calcium chloride gives a higher surface tension, as the curves indicate. A similar antagonistic action was observed also with mixtures of potassium and sodium chloride.

Handovsky¹ points out that it is better to consider the surface tension as a function of the concentration of one electrolyte while that of the other remains constant instead of considering it in its dependence on the total concentration. Recalculation of Neuschlosz's data from the former standpoint reveals only a slight change in surface tension in the region of high concentrations with the sodium-calcium mixtures; but for mixtures of sodium and potassium, the results after the recalculation differ from those of Neuschlosz; but in this case, also, there is no question that one salt cuts down the surface tension-raising action of the other.

If the change in surface tension of lecithin sol by the presence of electrolytes is the result of coagulation, as seems probable, the antagonistic action of mixtures is doubtless due, in large measure, to the effect of each cation on the adsorption of the other. Freundlich and Scholz² prefer to assume that hydration influences are chiefly responsible for the antagonistic action; but this viewpoint is not sufficiently definite to be helpful. In so far as the adsorption of the ions is determined by their hydration³ and that of the adsorbent, it is of course quite proper to say that cationic antagonism is determined by hydration influences.

IONIC ANTAGONISM IN BIOLOGICAL SYSTEMS

The behavior of colloidal solutions of such substances as arsenic trisulfide, copper ferrocyanide, and lecithin in the presence of salt pairs is of importance owing to the existence of what appear to be analogous phenomena in biological systems.

Almost 50 years ago, Ringer⁴ attempted to use a sodium chloride solution isotonic with the blood, for the continuous perfusion of the heart of a frog. This solution was unsatisfactory as the beats diminished gradually and ceased entirely after a few minutes. It was discovered that traces of the chlorides of calcium and potassium added to the salt solution gave a perfusion liquid capable of maintaining the heart beat at a satisfactory height for a considerable time. The so-called "Ringer's solu-

¹ *Pfluger's Archiv.*, **185**, 7 (1920).

² *Kolloidchem. Beihefte*, **16**, 267 (1922).

³ Cf. p. 254.

⁴ *J. Physiol.*, **3**, 380 (1880-82); **4**, 29, 222 (1882-83); **7**, 291 (1886).

tion" contains 0.13 molar sodium chloride, 0.0011 molar calcium chloride, and about 0.0002 molar potassium chloride.¹ Similarly, Jacques Loeb² found that the fertilized eggs of a sea urchin, *Fundulus Heteroclitus*, do not develop to embryos when transferred to a solution of sodium chloride having the same concentration as sea water; but the destructive action of the sodium chloride is neutralized by adding calcium chloride in the ratio of one or two mols of the latter to two hundred of the former. Small concentrations of many other divalent cations have an effect similar to calcium ion. It is a striking fact that the optimum ratio of sodium chloride to calcium chloride is approximately the same as it is in nature, in sea water, and in the blood of animals. A similar relationship obtains with certain plants. Thus Osterhout³ demonstrated that wheat grown in a solution containing 0.12 molar sodium chloride and 0.0012 molar calcium chloride develops extensive rootlets and shows other signs of healthy growth, whereas in solutions of either 0.12 molar sodium chloride or 0.0012 molar calcium chloride alone no growth occurs. Moreover, zoospores of *Vaucheria* grow rapidly in a solution of 0.1 molar NaCl and 0.001 molar CaCl₂ or even in pure water; but show no signs of growth in either 0.1 molar NaCl or 0.001 molar CaCl₂. Observations of a similar character have been made repeatedly by a number of other biologists⁴ so that the antagonistic action of salts on living organisms can be considered as one of the commonplaces of biological science.

The influence of salts on living cells appears to be closely related to their permeability. Osterhout⁵ studied the effect of various electrolytes on the conductivity of certain sea weeds such as *Laminaria*. Immediately after removal from sea water, he

¹ Bayliss: "Principles of General Physiology," 207 (1920).

² Am. J. Physiol., 6, 411 (1902); Pfluger's Archiv., 88, 68 (1901); LOEB and WASTENEYS: Biochem. Z., 31, 450; 32, 155; 33, 489 (1911); 39, 167 (1912); J. Biol. Chem., 21, 223 (1915); LOEB: Ibid., 32, 147 (1917); J. Gen. Physiol., 5, 231 (1922).

³ Plant World, 16, 129 (1913); J. Biol. Chem., 19, 335 (1914).

⁴ OSTWALD: Pfluger's Archiv., 106, 568 (1905); cf. LILLIE: Am. J. Physiol., 29, 372 (1912); J. Gen. Physiol., 3, 783 (1921); NETTER: Pfluger's Archiv., 198, 225 (1923); SPIRO: Schweiz med. Wochschn., 51, 457 (1922); UTIN: Chem. Zentr., III, 887 (1922).

⁵ Science, [2] 35, 112; 36, 350 (1912).

found the tissues to exhibit a practically constant resistance to the passage of the current; but on exposure to a comparable NaCl solution, the resistance decreased and to a comparable CaCl₂ solution, the resistance increased; while exposure to properly balanced mixtures containing 100 mols NaCl to 1 to 2 mols CaCl₂ caused no appreciable variation from the normal. If Laminaria is first immersed in a 2.5 per cent solution of pure sodium chloride the electrical conductivity is increased; on adding a little calcium chloride to the solution, the sea weed returns to normal conductivity without showing signs of permanent damage.¹ It appears, therefore, that the protoplasmic membrane is a physical system capable of undergoing reversible variations in permeability as a result of exposure to solutions containing varying amounts of sodium and calcium salts. From such observations, Osterhout² divides substances into two groups: (1) those which cause an increase in permeability and (2) those which can produce a decrease in permeability. From this point of view, substances belonging to the first class will antagonize those belonging to the second and *vice versa*.

The soundness of this point of view is indicated not only by the fact that we are able to predict both qualitatively and (to a considerable extent) quantitatively the effect of combinations of salts but also by the very significant fact that we are able to extend this conception to organic compounds and to show that non-electrolytes which decrease permeability can also antagonize such substances as NaCl. These facts indicate that the hypothesis may be applied in a general manner so as to include both electrolytes and non-electrolytes.

This hypothesis does not account for the change in permeability but Clowes³ has sought to explain it by comparing the cell membrane to an oil-water emulsion in which soaps concentrate at the interface between oil and water, lowering the surface tension of one or the other depending on whether the soap is oil soluble or water soluble.⁴ Thus we should expect an emulsion of oil in water in the presence of sodium salts and of water in oil in the presence of calcium salts.

¹ OSTERHOUT: *Science*, [2] 34, 187 (1911).

² *Science*, [2] 41, 255 (1915).

³ *J. Phys. Chem.*, 20, 407 (1916).

⁴ BANCROFT: "Applied Colloid Chemistry," 261 (1921).

Salts of calcium promote and alkalies and salts of sodium inhibit the transformation of a system consisting of a non-aqueous phase dispersed in water into the reverse type of systems, consisting of water more or less perfectly dispersed in a non-aqueous phase. If the analog of islands surrounded by water and lakes surrounded by land is considered, it will be obvious that a transformation has been effected from a system which is freely permeable to water to one which is impermeable, if the transformation is complete. Since the transformation in one direction is effected by salts of calcium and in the reverse direction by salts of sodium, any intermediate degree of permeability might well be obtainable by simply varying the proportions of the salts of sodium and calcium introduced into the system.

From this point of view, it would follow that the critical ratio of sodium and calcium salts is one which produces a balance between the two types of emulsion that is most favorable for life and growth. In support of his hypothesis, Clowes, working with oil, water, and soap, showed that the ratio of sodium and calcium salts necessary to produce a balancing between these two types of emulsions was about the same as that found in sea water. As already noted, Osterhout showed that the specific conductivity of *laminaria* is increased by the addition of sodium salts and decreased by the addition of calcium salts. Now, if one has a labile emulsion in a critical state, its conductivity should be increased by converting it chiefly into an emulsion of oil in water. Clowes¹ was able to duplicate Osterhout's results by impregnating filter paper with an emulsion of oil, water, and soap to which he afterwards added salts of sodium and calcium.

Although quite suggestive, Clowes' view that a cell membrane is a labile emulsion appears to be altogether inadequate to account for the marked osmotic pressure which a cell manifests. It seems better, at least for the present, to consider the cell membrane as a more or less rigid, semi-permeable pellicle comparable in certain respects to a copper ferrocyanide membrane.

From what we now know of the structure of jellies and gelatinous precipitates,² it seems probable that a copper ferrocyanide membrane consists of myriads of minute particles which adsorb water strongly. As a result of investigations carried out in

¹ Proc. Soc. Exp. Biol. Med., 15, 108 (1918).

² Cf. WEISER: Bogue's "Colloidal Behavior," 1, 377 (1924).

Bancroft's laboratory, Gurchot¹ considers a copper ferrocyanide film to be a negative colloidal film analogous to a colloidal sol. It is therefore a granular membrane, the space between the particles of which is more or less completely filled with adsorbed water. The film is therefore a dynamic system capable of reversible coagulation.

This concept of the nature of a copper ferrocyanide membrane enables one to account for a number of facts. To illustrate, it is known that below a certain concentration some salts will pass through a copper ferrocyanide membrane and sugar will not; while at higher salt concentrations, both will pass through. This is explained by assuming that no coagulation of the membrane takes place below a certain critical concentration of salt. The salts being soluble in water dissolve in the water layer and so pass through the membrane. Sugar molecules cannot go through in this way because of strong negative adsorption. When the salt concentration reaches the critical coagulation value, there results agglomeration of the particles which carry with them their film of adsorbed water leaving cracks through which the sugar can pass. Reversing the coagulation by adding a peptizing agent reforms the semipermeable film and the sugar will no longer pass through. Gurchot apparently succeeded in accomplishing this reversal in permeability to sugar after coagulation with alcohol and salts, by means of CuSO_4 . Potassium ferrocyanide would doubtless produce the same results in very low concentration.

If the membrane of a living cell is a colloidal film similar to a colloidal sol that can undergo reversible coagulation, there would appear to be a close analogy between the action of salt pairs in the precipitation of such sols as copper ferrocyanide and arsenic trisulfide and the antagonistic action of salt pairs on the permeability and hence on the life and growth of living cells. From this point of view, all of the factors influencing the precipitating action of salt pairs as it affects the stability of sols, which is outlined above, will be concerned in the antagonistic action of salt pairs as it affects the permeability of protoplasm.

¹ *J. Phys. Chem.*, **30**, 83 (1926).

V
COLLOIDAL SILICATES

CHAPTER XIX

SILICATE SOLS AND GELS

Of the methods that are employed for preparing salts in the colloidal state, but one seems to offer any particular promise as a means of forming silicate gels and sols. This is the condensation method by double decomposition of sodium silicate and salts of the heavier metals. The nature of the product obtained by this process will depend not only on the heavy metal entering into the reaction but, to a considerable extent, upon the nature of the sodium silicate solutions. Accordingly, special attention will be given first to the constitution and properties of such solutions.

SODIUM SILICATE SOLUTIONS

When reference is made to solutions of sodium silicate, one usually thinks of waterglass, which is not a solution of a definite chemical individual but is a variable system of the components sodium oxide, silica, and water. In commercial silicate solutions, the ratio of Na_2O to SiO_2 may vary from 1:1 to 1:4.¹ The 1:1 ratio, sodium metasilicate, is on the market as a crystalline powder. As a result of conductivity² and freezing-point³ measurements it has been claimed that dilute solutions of sodium silicate are practically completely hydrolyzed, yielding sodium and hydroxyl ions and colloidal hydrous silica, but no silicate ions. The presence of myriads of colloidal particles were observed by Stericker⁴ in an ultramicroscopic examination of solutions containing 18 to 35 per cent of commercial silicate in which the ratio $\text{Na}_2\text{O}:\text{SiO}_2$ was 1:3.3. The clearly distinguished particles were probably not very highly hydrous and were

¹ VAIL: *J. Ind. Eng. Chem.*, **11**, 1029 (1919).

² KOHLRAUSCH: *Z. physik. Chem.*, **12**, 773 (1893).

³ LOOMIS: *Wied. Ann.*, **60**, 523 (1897).

⁴ *Chem. Met. Eng.*, **25**, 61 (1921).

believed to consist of silica and soda stabilized by preferential adsorption of hydroxyl ion.

The investigations of Bogue¹ and the more recent observations of Harman indicate that dilute silicate solutions are hydrolyzed much less than formerly supposed and that the percentage hydrolysis is quite low in concentrated solutions.² Moreover, Harman gives extended experimental evidence of the existence of silicate ions in silicate solutions³ and of the absence of hydroxyl ion adsorption by colloidal particles of hydrous silica. The several lines of experimentation followed by Harman will be considered in the subsequent paragraphs.

Conductivity of Silicate Solutions.—Harman⁴ prepared pure crystalline sodium metasilicate, $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$, and from a solution of this salt he made solutions of varying ratios of $\text{Na}_2\text{O}:\text{SiO}_2$ by removing the alkali electrolytically.⁵ Solutions in which the ratio $\text{Na}_2\text{O}:\text{SiO}_2$ was 2:1 and 1:1 were found to be excellent conductors,⁶ while solutions, in which the ratio was 1:2, 1:3, and 1:4 were good conductors in dilute solution but abnormally low in concentrated solution. This is illustrated graphically in Fig. 33 in which the equivalent conductivity of solutions of various concentrations is plotted against the $\text{Na}_2\text{O}:\text{SiO}_2$ ratio. Considering dilute solutions, it will be seen that the conductivity of a caustic soda solution to which silica has been added decreases linearly and rapidly until the ratio 1:2 is reached, where there is a sharp change in direction, the conductivity again falling regularly and linearly but not so rapidly as in the less siliceous solutions. The sharp change in direction at the ratio 1:2 is taken to indicate the existence of a definite salt in solution. Since $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ is a well-defined crystalline salt, the absence of a break in the curve at 1:1 indicates that the salt is appreciably hydrolyzed in dilute solution and that the linear decrease in conductivity is due to the gradual disappearance of the mobile hydroxyl ion. The

¹ *J. Am. Chem. Soc.*, **42**, 2575 (1920).

² STERICKER: *Chem. Met. Eng.*, **25**, 61 (1921).

³ Cf., also, MAIN: *J. Phys. Chem.*, **30**, 535 (1926).

⁴ *J. Phys. Chem.*, **29**, 1155 (1925).

⁵ SPENCER and PROUD: *Kolloid-Z.*, **31**, 36 (1922); LOTTERMOSER: *Ibid.*, **30**, 346 (1922); KRÖGER: *Ibid.*, **30**, 16 (1922).

⁶ Cf., also, KOHLRAUSCH: *Wied. Ann.*, **47**, 756 (1892); Z. physik. Chem., **12**, 773 (1893); KAILENBERG and LINCOLN: *J. Phys. Chem.*, **2**, 77 (1898).

conductivity for ratios up to 1:2 are much greater than could result alone from hydrolysis into sodium hydroxide and colloidal hydrous silica. Above the ratio 1:2 where the hydroxyl ion

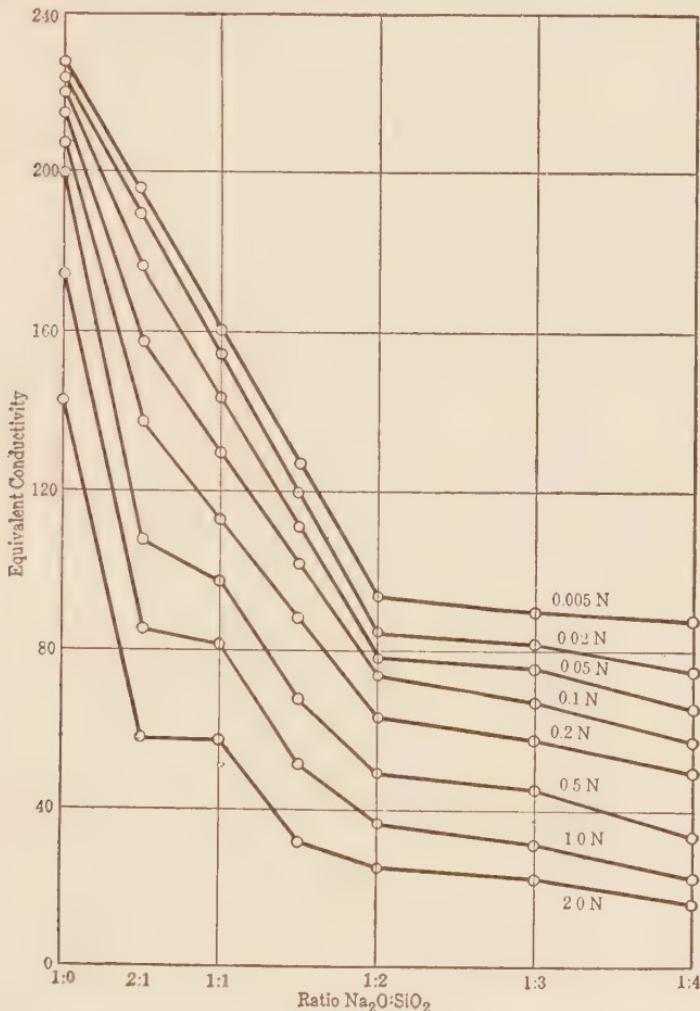


FIG. 33.—Equivalent conductivity against the $\text{Na}_2\text{O}:\text{SiO}_2$ ratio for solution of various concentrations.

concentration is very low, the sodium ion accounts for only about one-half of the observed conductivity. To account for the remainder, the obvious way is to postulate the existence of silicate ions with mobilities ranging from 40 to 60. It may be

mentioned at this point that the equivalent conductivity calculated from freezing-point, hydroxyl ion, and sodium ion measurements agrees well with conductivity data determined experimentally.

The curves for more concentrated solutions exhibit three changes of direction which might be taken to indicate the presence in solutions of a salt with the $\text{Na}_2\text{O} : \text{SiO}_2$ ratio 2:1 as well as 1:1 and 1:2. But since there is no independent evidence of the existence of salts with ratios other than 1:1 and 1:2, it is probable that other ratios are mixtures of these with sodium hydroxide or hydrous silica, as the case may be. To account for the relatively low conductivity of concentrated solutions above the ratio 1:2, Harman suggests that either the extent of ionization is too low, or aggregate or colloid formation takes place. As already pointed out, there is no doubt of the existence of colloidal particles in the more siliceous solutions.

Hydrolysis.—The hydrolysis of silicate solutions of varying concentrations and of varying $\text{Na}_2\text{O} : \text{SiO}_2$ ratios was determined electrometrically by Bogue¹ whose observations were confirmed in all essential respects by Harman.² The results of the latter are shown graphically in Fig. 34 in which the percentage hydrolysis calculated from the hydroxyl ion concentration as given by hydrogen electrode measurements, is plotted against the $\text{Na}_2\text{O} : \text{SiO}_2$ ratio. It will be seen that these data show the hydrolysis to be far from complete. Thus a 0.01 normal solution of Na_2SiO_3 is hydrolyzed to the extent of 27.8 per cent while ratios 1:3 and 1:4 at the same concentration show only 1.5 per cent hydrolysis. Moreover, the degree of hydrolysis falls off with increasing concentration for all ratios.

It is obvious that the correctness of the conclusions concerning the percentage hydrolysis depends upon the accuracy of the determination of the hydroxyl ion concentrations. It is assumed, of course, that the hydrogen electrode measurements give a true measure of the hydroxyl ion present in the system. This is probably not the case if a part of the hydroxyl ions are adsorbed by colloidal particles present in the system. It has been demonstrated that adsorbed chloride ion will not give a test with silver

¹ *J. Am. Chem. Soc.*, **42**, 2575 (1920).

² *J. Phys. Chem.*, **30**, 1100 (1926).

nitrate¹ and its effect on a chlorine electrode will be negligible. Similarly, it is extremely improbable that adsorbed hydroxyl ion would behave toward a hydrogen electrode in the same way as a free hydroxyl ion. The values of the hydrolytic dissociation

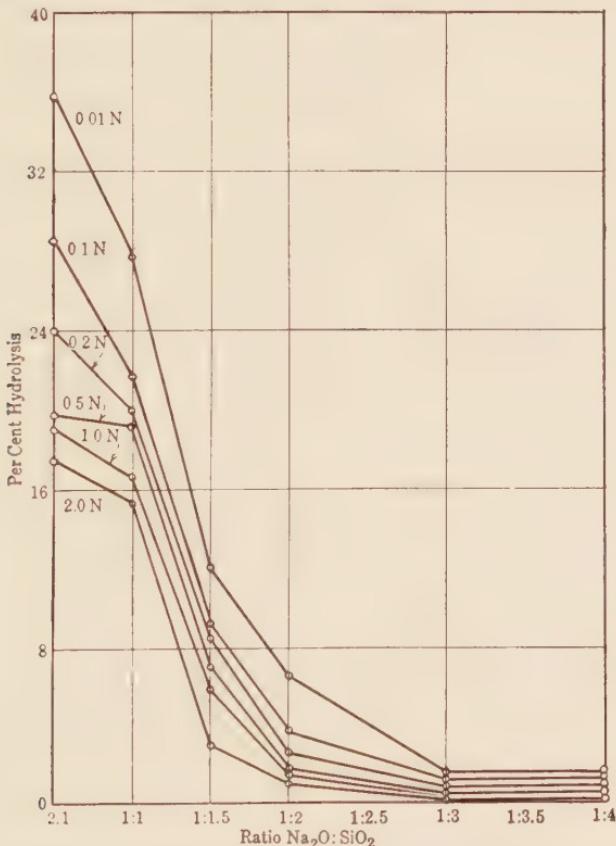


FIG. 34.—Per cent hydrolysis against the Na₂O:SiO₂ ratio for solutions of various concentrations.

determined from electromotive force measurements on a colloidal system, such as certain sodium silicate solutions, will be correct only in case no hydroxyl ion is adsorbed. As will be shown in the next section, it is not possible to account for the high osmotic activity of dilute sodium silicate solutions if it is assumed that the silica exists only as colloidal silica which has adsorbed

¹ RUER: *Z. anorg. Chem.*, **43**, 85 (1905).

hydroxyl ion. Accordingly, it is probable that Bogue's and Harman's determinations of percentage hydrolysis are approximately correct.

Osmotic Activity.—The osmotic activity of various sodium silicate solutions was determined by Harman¹ from measurements



FIG. 35.—Molecular lowering of the freezing point against the $\text{Na}_2\text{O}:\text{SiO}_2$ ratio for solutions of various concentrations.

of the lowering of the freezing point. In Fig. 35 the data for the molecular lowering of the freezing point $\frac{\Delta}{m}$ is plotted against the $\text{Na}_2\text{O}:\text{SiO}_2$ ratio for solutions of varying concentrations. It will be seen that ratios 2:1 and 1:1 and to a lesser degree 1:2, exhibit a high degree of osmotic activity especially in dilute solutions. Moreover, ratios 1:3 and 1:4 show a relatively high

¹ *J. Phys. Chem.*, **31**, 355 (1927).

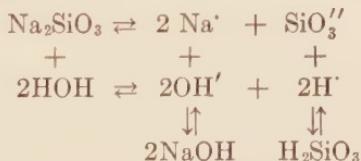
osmotie activity in dilute solutions as compared with the low value in concentrated solutions.

If the van't Hoff factor i is calculated for the solutions in which the $\text{Na}_2\text{O}:\text{SiO}_2$ ratio is 1:1 using the expression $i = \frac{\Delta}{m} \times 1.858$,¹ a fairly high degree of hydrolysis or ionization is indicated, even in the more concentrated solutions. In a 0.01 normal solution, the value for n comes out to be 3.87 which lies between 3, expected if total ionic dissociation takes place, and 4, the consequence of total hydrolytic dissociation and ionization of the hydroxide formed, assuming in the latter case that all the silica is colloidal and is without influence on the other constituent of the solution. If the laws of ideal solutions are assumed to apply in this case the percentage hydrolysis is $\frac{3.87}{4} \times 100 = 97$ per cent which agrees well with the figure calculated from conductivity measurements of both Harman and Kohlrausch and from the freezing-point measurements of Loomis.²

Since the percentage hydrolysis by electrometric measurements is 27.8 per cent and from freezing-point and conductivity data is 97 per cent, Harman³ concludes that neither

. . . (1) 27.8 per cent hydrolytic dissociation into $2\text{Na}^+ + 2\text{OH}^- + \text{colloidal H}_2\text{SiO}_3$ alone occurs, as this does not agree with the freezing-point results, nor (2) is the silica or silicic acid formed, wholly, if at all, colloidal, *i.e.*, SiO_3 ions must exist in the solution, and both hydrolytic and ionic dissociation must take place.

The interaction of sodium metasilicate and water may be represented as follows at very low concentration, where if hydrolysis has taken place in two stages the concentration of HSiO_3' will be negligible:

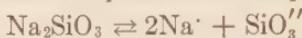


¹ 1.858 is the molecular lowering of an ideal substance at infinite dilution.

² Wied. Ann., 60, 523 (1897).

³ J. Phys. Chem., 31, 369 (1927).

From electromotive force measurements there is 27.8 per cent hydrolytic dissociation at concentration 0.005 m (or $N_w = 0.01$). From sodium ion measurements there is 97.5 per cent of the primary reaction



at this concentration. The H_2SiO_3 formed, as indicated above, may be taken as all crystalloidal, which seems justifiable at this low concentration, and be capable of dissociating into H^+ and SiO_3^{2-} ions, a reasonable possibility in spite of the general belief to the contrary, and one which receives so much support from experimental evidence based upon conductivity measurements, transport number experiments, diffusion experiments, apart from the favorable evidence adduced herein, that it appears almost a certainty. Calculating the van't Hoff factor i upon this basis and making use of the OH^- and Na^+ ion concentration, we get $i = 3.52$, where i from freezing points, is equal to 3.87.

This is fairly good agreement, considering that it depends on ordinary laboratory freezing-point technique, and on two independent sets of electromotive force measurements, and it not only supports the view that both hydrolytic and ionic dissociation takes place but that a fairly correct percentage value has been obtained for both these dissociations.

Let us consider almost complete hydrolysis into NaOH and colloidal H_2SiO_3 , according to the theory put forward by Kohlrausch¹ and by Loomis,² the extent of such hydrolysis, to be determined by the concentration of sodium ions,³ but assuming the OH^- ions to be adsorbed to a large extent by the colloidal silica so that the actual OH^- ion concentration agrees with the percentage hydrolysis found by e.m.f. measurements. On this basis, for concentration $N_w = 0.01$, i.e., 0.005 m , $i = 2.53$, whereas from freezing-point measurements i is 3.87. This non-agreement, clearly outside the bounds of experimental error, appears to afford definite proof against OH^- ion adsorption.

From similar considerations, Harman concludes that the solutions in which the $\text{Na}_2\text{O}:\text{SiO}_2$ ratio is 1:2 do not contain the salt $\text{Na}_2\text{Si}_2\text{O}_5$ but rather NaHSiO_3 which behaves like Na_2SiO_3 in giving rise to Na^+ , OH^- , and HSiO_3^- ions together with H_2SiO_3 . Electrometric titration of sodium silicate solutions likewise indicates that silicic acid is a dibasic acid giving salts NaHSiO_3 and Na_2SiO_3 .⁴ The 1:3 and 1:4 ratios, on the other hand, do not appear to be definite salts but rather to consist of

¹ *Z. physik. Chem.*, **12**, 773 (1893).

² *Wied. Ann.*, **60**, 531 (1897).

³ HARMAN: *J. Phys. Chem.*, **30**, 922 (1926).

⁴ HARMAN: *J. Phys. Chem.*, **31**, 616 (1927).

complex aggregates and ionic micelles which are assumed tentatively to have the composition $[m \text{ SiO}_3, n \text{ SiO}_2 \text{ aq}]^{m''}$.

The ultramicroscope definitely discloses the presence of colloidal particles in the more siliceous mixtures. Since some silicate ions exist in such solutions, the colloidal particles derive their negative charge from adsorption of these ions giving what may be termed colloidal ions or ionic micelles; but, in my opinion, such colloidal particles differ in no essential way from colloidal arsenic trisulfide particles stabilized by preferential adsorption of HS' ions or of colloidal gold particles stabilized by preferential adsorption of hydroxyl ions.

Transport Numbers of the Ions.—Harman¹ determined the transport numbers of the ions in various silicate solutions by the Hittorf method, both electrode portions being analyzed for both sodium and silica. The transport number, T. N., of the silicate ion was calculated from the expression

T. N. (Silicate ion) =

$$\frac{\text{total change in weight of SiO}_2}{N \times (\text{weight of SiO}_2 \text{ equivalent to Ag deposited in coulometer})}$$

where N is the number of mols per divalent charge, $2F$, of the anion; and the weight of "SiO₂ equivalent to the Ag deposited" is calculated from the relation, 1 Ag equivalent to $\frac{1}{2}\text{SiO}_2$. The average value of N is equal to the molar ratio $\frac{\text{SiO}_2}{\text{Na}_2\text{O}}$ in the solution.

In Table XLIX are given the transference numbers of the ions in solutions with different ratios of Na₂O:SiO₂. These results indicate that a fair proportion of the current, at least one-half

TABLE XLIX.—TRANSFERENCE NUMBERS OF IONS IN SODIUM SILICATE SOLUTIONS

Ratio Na ₂ O + SiO ₂	N_{Na}	N_{silicate}	$N_{\text{OH}} = 1 - (N_{\text{Na}} + N_{\text{silicate}})$
1:1	0.37	0.16	0.53
1:2	0.41	0.41	0.18
1:3	0.43	0.46	0.11
1:4	0.48	0.59	

¹ *J. Phys. Chem.*, **30**, 359 (1926).

in the most siliceous mixtures, is carried by the silica. Harman recognized two possibilities: either the silica exists as ions, or hydroxyl ions are adsorbed on colloidal particles giving the necessary charge to the silica. Since the view that the silica exists chiefly as colloidal particles that have adsorbed hydroxyl ions is incompatible with the high osmotic activity of dilute silicate solutions, the only conclusion is that the silica must exist as ions.

Diffusion.—The existence of silicate ions and of crystalloidal H_2SiO_3 in silicate solutions is further indicated by diffusion experiments of Harman¹ using membranes of collodion and parchment paper. For example, most of the silica in 0.3 normal solutions containing Na_2O and SiO_2 in the ratio 1:1 and 1:2 was diffusible. Moreover, two-thirds of the silica in 0.3 normal and one-third of the silica in 1 normal solutions of the 1:4 ratio diffused through the membranes. In very dilute solutions of all ratios, the silica behaved as if it were in true solution.

While the work of Harman has extended our knowledge of the nature of sodium silicate solutions, one is left with the impression that an important factor in the behavior of such solutions is not taken into account, namely the effect of ageing. Mylius and Groschuff² are of the opinion that at the moment of its formation from waterglass, silicic acid exists as such in a molecular solution which passes unchanged through a dialyzing membrane; and that the colloidal state results from polymerization of the acid with the splitting off of water. In commenting on this view a short time ago,³ it was suggested that the newly formed silicic acid was colloidal but the primary particles were too finely divided to be stopped by the membrane employed. After a time, however, these very highly dispersed particles coalesced to form larger primary particles with the loss of adsorbed water as a result of the decrease in specific surface. In the light of Harman's work, it now appears that silicic acid, as such, exists in solution as Mylius and Groschuff assumed. There is no doubt, however, that such a solution goes over in time to the colloidal state and that the particles of colloidal silica agglomerate and age slowly.

¹ *J. Phys. Chem.*, **31**, 616 (1927); cf., also, GANGULY: *Ibid.*, **31**, 407 (1927).

² *Ber.*, **39**, 116 (1906).

³ WEISER: "The Hydrous Oxides," 194 (1926).

but continuously¹ approaching crystalline SiO_2 as a limit.² So far as the author is aware, the experiment has not been tried, but one should expect to find ultramicrons, even in dilute solutions of the definite salt Na_2SiO_3 , if the latter were allowed to stand for a long time. Since everybody recognizes the existence of colloidal silica in more siliceous solutions, it is obvious that the system when first prepared is not in equilibrium, attaining this condition only after long standing, if at all. The tendency of colloidal silica particles to coalesce into larger aggregates and finally to gel, is clearly recognized by Vail³ as one of the outstanding characteristics of silicate solutions containing colloidal silica.

SILICATE SOLS

Since sodium silicate solutions contain silicate ions, together with varying amounts of colloidal silica, it should be possible to prepare silicate sols of varying purity by double decomposition of very dilute solutions of sodium silicate and salts of heavier metals. Ota and Noda⁴ prepared such sols by the addition of a dilute waterglass solution to dilute solutions of copper, silver, magnesium, zinc, aluminum, titanium, manganese, ferrous iron, and cobalt. While a part of the colloidal material in such preparations is the metallic silicate, such salts will hydrolyze to a greater or lesser extent, giving a mixture of the hydrous oxide of the metal and hydrous silica. It seems altogether unlikely, for example, that any titanium silicate should exist in contact with water.

The colloidal mixtures of silicates and hydrous oxides exert an enzymic action like an oxidase when examined by the indophenol reaction. The order of activity of the silicate sols is: $\text{Ag} > \text{Cu} > \text{Co} > \text{Ti} > \text{Al} > \text{Mn} > \text{Zn} > \text{Mg} > \text{Fe}''$. Powdered kaolin, talc, and serpentine do not exhibit this action. Natural earths

¹ Cf. SCHWARZ and STÖWENER: *Kolloidchem. Beihefte*, **19**, 171 (1924); SCHWARZ and LIEDE: *Ber.*, **53**, 1509, 1680 (1920); SCHWARZ: *Kolloid-Z.*, **28**, 77 (1921); GRUNDMANN: *Kolloidchem. Beihefte*, **18**, 197 (1923).

² Cf. BACHMANN: *Z. anorg. Chem.*, **100**, 1 (1917); ZSIGMONDY-SPEAR: "Chemistry of Colloids," 137 (1917); SCHWARZ and STÖWENER: *Kolloidchem. Beihefte*, **19**, 171 (1924).

³ *J. Soc. Chem. Ind.*, **44**, 214 T (1925).

⁴ *J. Sci. Agr. Soc., Japan*, **258**, 287 (1924).

show a weak activity compared to the artificial preparations. This behavior recalls the oxidase-like action of colloidal manganese dioxide toward guiac tincture, hydroquinone, etc.¹

SILICATE GELS

When solutions, not too dilute, of sodium silicate and the salt of a heavy metal are allowed to interact, a gelatinous precipitate is obtained which will vary widely in composition depending on the $\text{Na}_2\text{O} : \text{SiO}_2$ ratio in the silicate solution, the nature of the heavy metal, the concentration of the solutions, and the relative proportions of the reacting materials.² In general, one might expect the gel to contain considerable silicate with salts of the alkaline earths;³ some silicate with such salts as copper, cobalt, and nickel;⁴ and little or no silicate with salts of ferric iron, chromium, or aluminum. With the latter salts, the gelatinous mass will probably consist almost entirely of hydrous oxides of the trivalent metal and hydrous silica.

The gels formed on mixing waterglass and solutions of the chlorides of aluminum, chromium, calcium, copper, and nickel readily part with the metallic oxide, leaving pure silica on treating the dried preparations with hydrochloric acid.⁵ By this procedure a silica gel with superior adsorbing qualities may be prepared.

Lloyd⁶ prepared from fuller's earth an aluminum silicate gel which adsorbs alkaloids strongly from either neutral or acid solutions thereof. The adsorbed alkaloid may be recovered by treatment with an alkaloid solvent. It has been suggested that the material be called Lloyd's reagent.⁷

Base-exchange Silicate Gels.—Silicate gels are known which have the power to a marked degree of taking up the cation of any

¹ SJOLLEMA: *Chem. Weekblad.*, **6**, 287 (1909); *Chem. Zentr.*, I, 496 (1911).

² Cf. JORDIS and HENNIS: *J. prakt. Chem.*, [2] **77**, 240 (1908).

³ JORDIS and KANTER: *Z. anorg. Chem.*, **35**, 90, 344 (1903); **42**, 418 (1904); **43**, 48, 314 (1905); LE CHATELIER: "Recherches expérimentales sur la constitution des mortieres hydrauliques," Paris, (1887).

⁴ SCHWARZ and MATHIS: *Z. anorg. Chem.*, **126**, 55 (1923).

⁵ HOLMES and ANDERSON: *J. Ind. Eng. Chem.*, **17**, 280 (1925).

⁶ U. S. Patent, 1048712 (1912).

⁷ WALDBOTH: *J. Am. Chem. Soc.*, **35**, 837 (1913).

electrolyte from solution and, at the same time, returning to the solution an equivalent amount of another cation originally contained in the gel. An important example of this class of substances is the amorphous permutits (from *permutare*, to change) first prepared by Gans¹ by fusing together a mixture of china clay, sodium carbonate, and quartz, followed by leaching the vitreous mass with water. The product obtained in this way is a highly porous, amorphous gel which corresponds approximately to the formula $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot x\text{H}_2\text{O}$. It may be an amorphous aluminum silicate similar in constitution to the naturally occurring crystalline zeolite of the same composition.

If water containing calcium or magnesium chloride is allowed to percolate through a column of sodium permutit, there results a solution of sodium chloride free from calcium or magnesium and calcium or magnesium permutit is formed. The original permutit is restored by percolating a concentrated solution of sodium chloride through the alkaline earth permutit, whereby the calcium or magnesium is replaced by sodium. This base exchange is the basis of the permutit process for softening hard water. If sodium or calcium permutit is treated with a solution of a manganese salt, a manganese permutit is produced; and if a solution of potassium permanganate is employed, a potassium-manganese permutit results, covered with a finely divided layer of a higher oxide of manganese. This product is employed to remove iron from water as well as for oxidizing organic matter and bacteria in water. Regeneration is accomplished by treatment with a solution of potassium permanganate.

In many cases, the exchange of cations takes place almost quantitatively. Thus, a sodium permutit in contact with a moderately concentrated silver nitrate solution was found by Günther-Schulze² to have exchanged 96.5 per cent of its sodium for silver in a day's time. The extent and rate of the exchange depends in large measure on the physical character of the permutit. Thus, a freshly prepared sample exchanges bases more completely and quickly than a dried one.³

¹ *Jahrber. Königl. Preuss. Geol. Landesanstalt*, **26**, 175 (1905); **27**, 63 (1906).

² *Z. physik. Chem.*, **89**, 168 (1915).

³ BEUTELL and BLASCHKE: *Centr. Mineral. Geol.*, 142 (1915).

A special siliceous gel known as "doucil" has been prepared¹ by mixing solutions of sodium silicate and sodium aluminate, drying and washing to remove soluble sodium salts. The dried gel has the approximate composition $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$ corresponding to the natural crystalline zeolite, phillipsite. Like the zeolites and the artificial permutits, doucil may be employed to soften water and to recover either alkali or alkaline earth metals from dilute solutions.² Unlike other base-exchange silicates, doucil has a very minute gel structure possessing pores of ultramicroscopic dimensions. It therefore exhibits a relatively high exchange capacity for a given mass. "Its high capacity and quick regeneration fits it especially for small domestic softening units although it has given excellent results in large industrial units especially designed to take advantage of its properties."³

Reference to base-exchange materials naturally raises the question of the mechanism of the cation transfer. It was at first believed that the process is a typical reversible chemical reaction in which the equilibrium conditions can be expressed by means of the mass law.⁴ Subsequent observations indicate that this is not the case. Wiegner⁵ points out that the behavior of base-exchange gels in contact with a neutral solution has all the characteristics of an exchange adsorption process. Cations are taken up from the salt solution by the gel in exchange for equivalent amounts of other ions. The equilibria are frequently set up smoothly and quickly as in the case of adsorption. Moreover, if the amount of cations taken up by a unit amount of silicate is plotted against the equilibrium concentration of the surrounding solutions, a typical adsorption curve is obtained

which fits the Freundlich equation $\frac{X}{M} = Kc^n$.

¹ WHEATON: English Patent, 177746 (1922); U. S. Patent, 1586764 (1922).

² VAIL: *Trans. Am. Inst. Chem. Eng.*, [2] **16**, 119 (1924).

³ VAIL: *J. Soc. Chem. Ind.*, **44**, 214 T (1925).

⁴ GANS: *Jahrber. Königl. Preuss. Geol. Landesanstalt*: **26**, 179 (1905); **27**, 63 (1906); GÜNTHER-SCHULZE: *Z. physik. Chem.*, **89**, 168 (1914); *Z. Elektrochem.*, **28**, 85 (1922); RAMANN and SPENGEL: *Z. anorg. Chem.*, **105**, 82 (1918).

⁵ *J. Landw.*, **60**, 111, 197 (1912); ROSTWOROWSKI and WIEGNER: *Ibid.*, **60**, 223 (1912); *Kolloid-Z. (Zsigmondy Festschrift)* **36**, 341 (1925).

Wiegner¹ has recently modified the Freundlich adsorption isotherm into an exchange isotherm as follows:

$$y = K \left(\frac{c}{a - c} \right)^{\frac{1}{n}}$$

in which y is the amount in milliequivalents exchanged by 1 gram

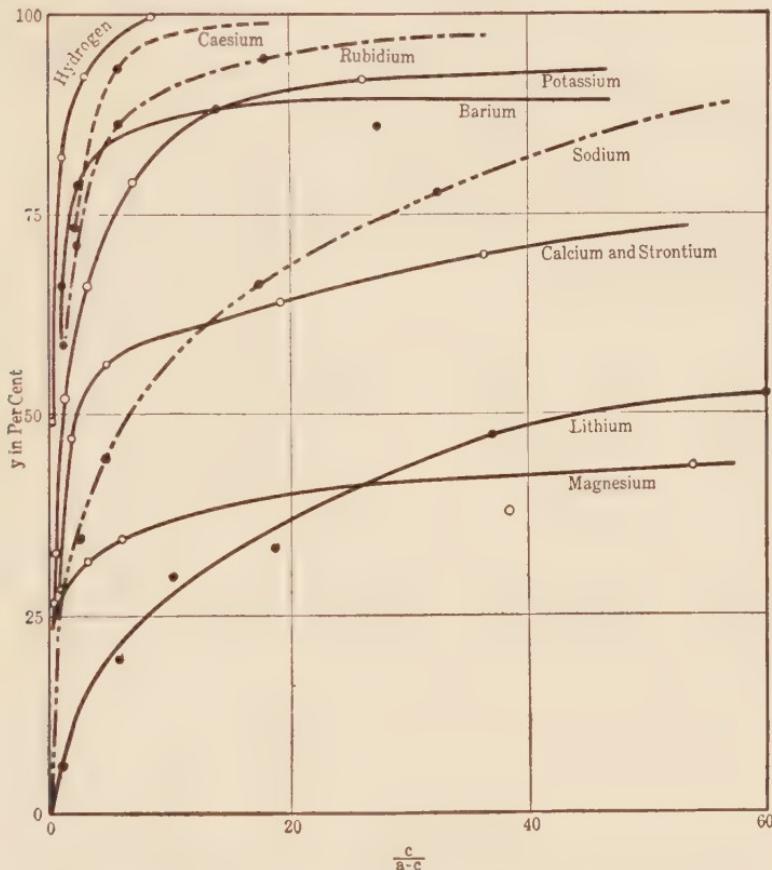


FIG. 36.—Curves showing the exchange of ions with ammonium permumit.

of gel, a the concentration of the original solution, and c the concentration after equilibrium is reached expressed in milliequivalents; K and n are constants. Some typical exchange curves² for univalent and bivalent ions with ammonium permumit

¹ JENNY and WIEGNER: *Kolloidchem. Beihefte*, **23**, 443 (1926).

² JENNY and WIEGNER: *Kolloidchem. Beihefte*, **23**, 428 (1926); WIEGNER and JENNY: *Kolloid-Z.*, **42**, 268 (1927).

as the base-exchange gel are given in Fig. 36 in which y in per cent is plotted against $\frac{c}{a - c}$. It will be seen that the capacity of the ions to enter the gel and displace the ammonium ion is the reverse of the lyotropic series for both groups of ions: Mg < Ca < Sr < Ba and Li < Na < K < Rb < Cs < H. In view of this relationship, it is believed that hydration may be an important factor in determining the base-exchange capacity of an ion just as it has been found to be in other adsorption phenomena.¹

With increasing hydration of univalent ions, the tendency to enter the gel falls off and the ease of displacement from the gel increases. The behavior of the divalent ions, on the other hand, is anomalous in certain respects. In high concentrations a univalent ion enters the gel more readily than the divalent ion which is hydrated to a similar degree. Thus the lithium curve lies slightly above the magnesium curve, the sodium curve above that for calcium and strontium, and the potassium curve above that for barium. But at low concentrations magnesium enters the gel more readily than lithium, calcium and strontium more readily than sodium, and barium more readily than potassium. Indeed with $N/100$ solutions all the divalent ions enter the gel more readily than any of the univalent ions. Thus the strongly hydrated magnesium ion is taken up more strongly than the very slightly hydrated potassium ion. Moreover, the divalent ions are always retained more tenaciously than the univalent ions. The anomalous behavior of the series of divalent ions, as compared with the series of univalent ions, is attributed to the formation of insoluble hydroxides with the hydroxyl ions adsorbed on the surface of the gel. Hence, magnesium ion which forms the relatively insoluble magnesium hydroxide is retained by the gel more strongly than other ions although its volume as determined by its degree of hydration cuts down its tendency to enter the gel and displace therefrom a smaller, less hydrated ion.

If one objects to considering the base exchange in silicate gels as an adsorption phenomenon, the alternative position is to regard a mixed base-exchange gel as a single-phase solid solution.²

¹ Cf. p. 254.

² Cf. ROTHMUND and KORNFELD: *Z. anorg. Chem.*, **103**, 129 (1918); **108**, 215 (1919); **111**, 76 (1920).

In accord with this view, we have seen that silver or calcium ions in suitable concentration replace sodium practically completely from a sodium permutit. Since the sodium is not confined to the surface, it is evident that the displacing cation must penetrate the entire mass, replacing the sodium atoms of each molecule. If the replacement is complete, the product is homogeneous; and if the replacement is incomplete, the intermediate product would appear to be homogeneous as is a solution. But, as Freundlich¹ points out, it is still questionable whether this should be regarded as something essentially different from adsorption since the forces which hold the solution molecules together are of the same nature as those acting in the case of adsorption.

Rothmund and Kornfeld call attention to the fact that it is more nearly correct to refer the results to the ratio of the two ions which enter into exchange rather than to the concentration of one ion, since for every ion taken up an equivalent amount of another ion enters the solution. In this respect the exchange of ions in permutit does not differ from polar exchange adsorption such as one encounters with arsenic trisulfide and the hydrous oxide mordants.² Rothmund and Kornfeld regard the base exchange as a solid solution phenomenon and from this viewpoint deduce the following equation for ions of equal valence at complete dissociation

$$\frac{c_1}{c_2} = k \frac{C_1}{C_2}$$

where c_1 and c_2 are the concentrations of the two ions in the solid phase and C_1 and C_2 are the concentrations of the corresponding ions in the solution. According to this equation, which applies through a limited range, the equilibrium is independent of the volume and therefore remains unchanged whether liquid be added or removed. The general relationship between the amount taken up and the equilibrium concentration of the solution is given by the empirical expression

$$\frac{c_1}{c_2} = k \left(\frac{C_1}{C_2} \right)^{\frac{1}{n}}$$

where c and C have the same significance as above, and k and n are constants. It will be noted that this equation corresponds

¹ "Colloid and Capillary Chemistry," 215 (1926).

² Cf. WEISER and PORTER: *J. Phys. Chem.*, **31**, 1828 (1927).

to that for the adsorption isotherm. Moreover, the exponent lies between 0.3 and 0.7, as in many typical cases of adsorption.¹

Since it is not possible to distinguish the exchange of bases by permutits and related substances from exchange adsorption, it must remain a moot question, for the present, whether the phenomenon should be interpreted as a case of adsorption or of solid solution.²

"Silicate Garden."—When small crystals of various readily soluble salts such as cobalt nitrate, copper sulfate, ferrous sulfate, nickel sulfate, manganese sulfate, zinc sulfate, cadmium nitrate, etc. are dropped into a silicate of soda solution of the right concentration and alkalinity, growths resembling plant shoots spring up, giving rise to the so-called "silicate garden," "artificial vegetation," or "colloidal forest."³ When the soluble crystal comes in contact with the silicate solution, it is quickly surrounded by a semipermeable siliceous gel. Diffusion then takes place through the gel membrane producing pressure inside the envelope which is distorted or broken depending on the rigidity of the structure which, in turn, depends on the concentration of the silicate solution and the nature of the metallic salt. The water which passes through the membrane dissolves more salt and a new wall is formed around the extruded solution. This process continues, giving rise to a great variety of curious shapes and forms which differ markedly with different metals. For example, hair-like filaments result with cadmium salts, and thick fungoid growths with nickel salts. The development of the plant-like shoots is more rapid in dilute than in concentrated silicate solutions up to the point where the gel is not sufficiently rigid to retain its form, and is more rapid in solutions where the Na_2O to SiO_2 ratio is high than in the more siliceous solutions. The gels consist of the hydrous oxides of the metals and hydrous silica or of a mixture of these with hydrous metallic silicates.

The colloid chemistry of clay and of glass will be considered in some detail in the two succeeding chapters.

¹ Cf. FREUNDLICH: "Capillary and Colloid Chemistry," 175 (1926).

² See, also, BIESALSKI: *Z. anorg. Chem.*, **160**, 107 (1927).

³ BÖTTGER: *J. prakt. Chem.*, [1] **10**, 60 (1837); MULDER: *Ibid.*, **22**, 41 (1846); DOLLFUS: *Compt. rend.*, **143**, 1148 (1906); ROSS: *Proc. Roy. Soc., N. S. Wales*, **44**, 583 (1910); *J. Chem. Soc.*, [2] **102**, 49 (1912).

CHAPTER XX

THE COLLOID CHEMISTRY OF GLASS

It has been generally assumed that the art of making glass arose in Egypt 6000 years ago. This is evidenced by representations of the art of glass blowing in the walls of the tomb of Tih (about 3800 B. C.) and the discovery of beads and other ornaments of glass among the ruins of ancient Memphis. Glass articles were first brought into Greece and Rome by the Phoenicians, who also learned how to make glass at an early date. Indeed, the cities of Tyre and Sidon were almost as famous for their glass as for the brilliant purple dye which colored the robes of kings. In the Roman Empire the manufacture of glass was taken up on a large scale by Tiberius Caesar, who imported Egyptian workmen into Rome and built up an industry rivaling that of Alexandria. The Roman glass was far from perfect, possessing a green or yellow tint and containing numerous small blowholes and nodules. Accordingly, it was usually colored deeply or rendered opaque by the addition of suitable materials and was employed for decorative purposes in mosaics and for jewelry. The excavations at Pompeii, however, reveal that glass was employed for windows to a limited extent as early as the first century of our era. With the downfall of the Roman Empire, the manufacture of glass was taken up in Constantinople and the Mohammedan orient where it flourished for five centuries. The art returned to Europe during the Middle Ages, centering in Venice; and, during the sixteenth and seventeenth centuries, Venetian glass became famous throughout the civilized world. From Italy the art spread to France and Germany and England.

In America the first glass factory was built at Jamestown in 1607, to make bottles; and 15 years later a second factory was built to make beads for commerce with the Indians. Both factories were destroyed in 1622 and it was not until late in the following century that the industry assumed any importance.

With this brief account of the discovery and spread of the art of glass making, we can proceed to a consideration of the nature and properties of this substance whose importance to art and science alike is difficult to overestimate.

COMPOSITION AND PROPERTIES OF GLASS

The substances known as glass differ widely in composition and properties. The simplest commercial glass is fused silica but most glasses consist of at least three major components and in some cases of twelve or more. The materials which are fused together to form glass fall into three general classes: (1) carbonates of the univalent metals, usually sodium, potassium, and lithium; (2) oxides or carbonates of divalent or trivalent metals of which calcium, lead, barium, and aluminum are the most important; and (3) oxides or other compounds of non-metals such as silica, boron, phosphorus, and arsenic.

Since the properties of a glass depend, to a large extent, on the composition, this varies with the purpose for which the glass is intended. The three most common types of glass are crown, Bohemian, and flint. Crown is the ordinary soda-lime-silica glass which is characterized by its low fusibility and ease of working. It is employed in making such articles as window glass, plate glass, and common laboratory apparatus. Bohemian glass is a potash-lime-silica product which fuses at a higher temperature and so is employed for making chemical apparatus, combustion tubes, etc. Flint glass is a potash-lead oxide-silica glass containing little or no lime. It is very fusible and possesses a high index of refraction which renders it valuable for making optical apparatus, tableware, artificial gems, etc. In the so-called borosilicate glasses, boric acid is added at the expense of soda in ordinary glass, and the silica content is high. An outstanding example of this type of glass is pyrex, which is characterized by its low temperature coefficient of expansion and its high resistivity to the action of chemical reagents, especially acids.

Attempts have been made to correlate the various physical properties of glass with composition. Thus, an additive relationship has been found to exist, within limits, between composi-

tion and such properties as thermal expansion,¹ density,² thermal conductivity,³ tensile strength,⁴ compressibility,⁵ specific heat,⁶ Young's modulus of elasticity,⁷ hardness,⁸ and refractive index.⁹ The simplicity of these relationships in practice makes it possible to prepare glasses of approximately known properties by bringing together suitable oxides in the requisite proportions. Thus, the preparation of a glass with a specified density or refractive index is simplified by the general additive relationships which subsist.¹⁰ It should be emphasized, however, that the formulas used in calculating the numerical values of a given property of a glass from the composition contain constants which are purely empirical and vary with the working conditions. Thus, while tables and diagrams from which the physical constants of a glass of known composition can be predicted are of great aid to the glass manufacturer, the theoretical significance of the additive relationships is by no means clear.

The existence of so many approximately additive properties of glass might lead one to suppose that the composition is quite simple. As a matter of fact, Sosman¹¹ and Tammann¹² suggest that in glasses the oxides themselves may exist as a result of dissociation of compounds. Definite evidence of the existence

¹ WINKELMANN and SCHOTT: *Wied. Ann.*, **51**, 730 (1894); ENGLISH and TURNER: *J. Soc. Glass Tech.*, **5**, 121 (1921); *J. Am. Ceram. Soc.*, **10**, 551 (1927).

² WINKELMANN and SCHOTT: *Wied. Ann.*, **51**, 697, 730 (1894); BAILLIE: *J. Soc. Chem. Ind.*, **40**, 141 T (1920).

³ WINKELMANN: *Wied. Ann.*, **67**, 794 (1899); WILLIAMSON and ADAMS: *Phys. Rev.*, [2] **14**, 99 (1909); BRIDGMAN: *Am. J. Sci.*, [5] **7**, 81 (1924).

⁴ WINKELMANN and SCHOTT: *Loc. cit.*

⁵ ADAMS and WILLIAMSON: *J. Franklin Inst.*, **195**, 475 (1923); BRIDGMAN: *Am. J. Sci.*, [5] **10**, 359 (1925).

⁶ WINKELMANN: *Wied. Ann.*, **49**, 401 (1893).

⁷ WINKELMANN and SCHOTT: *Loc. cit.*; WILLIAMS: *J. Am. Ceram. Soc.*, **6**, 980 (1923).

⁸ AUERBACH: *Wied. Ann.*, **43**, 61 (1891); **45**, 262, 277 (1892); **53**, 100 (1899).

⁹ TILLOTSEN: *J. Ind. Eng. Chem.*, **4**, 246 (1912); CLARKE and TURNER: *J. Soc. Glass Tech.*, **4**, 111 (1920).

¹⁰ Cf. ZSCHIMMER: *Sprechsaal*, **59**, 249, 265, 282, 297 (1926); *Chem. Abstr.*, **21**, 2765 (1927).

¹¹ *J. Franklin Inst.*, **194**, 741 (1922).

¹² *Z. anorg. Chem.*, **125**, 301 (1922).

of silicates in transparent glass has yet to be established and it has been suggested that such compounds are formed only at the moment of their separation from glass in the form of crystals. Thus, the specific volume curve for mixtures of magnesium and calcium silicates shows a definite break for the crystalline mixture but not for the glasses containing the same components in the same proportion. On the other hand, in the simple system sodium oxide-silica, when the specific volume and also the specific refraction are plotted against the composition, a definite break occurs in each case at a point corresponding to $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ ¹ and this particular compound has been isolated from melts and definitely characterized.² Moreover, a large number of silicates have been isolated from silicate fusions containing the oxides employed in fabricating commercial glasses. Thus, Morey and Bowen³ obtained not only the simple silicates $\text{Na}_2\text{O} \cdot \text{SiO}_2$, $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$, and $\text{CaO} \cdot \text{SiO}_2$ but also a series of complex compounds which are characterized by extensive dissociation when liquefied. It is probable, therefore, that such compounds exist in glasses, but lack of definite knowledge has led to the commendable plan of reporting the composition in terms of the oxide components instead of attempting to assign a definite formula to a body which may be a complex mixture of compounds.

THE COLLOIDAL NATURE OF GLASS

Glass in its rigid form is commonly regarded as a supercooled liquid. This view is based largely on the assumption that its properties change continuously with change in temperature. As a matter of fact, however, this assumption has been based almost entirely on qualitative observations and it is only in recent years that more refined studies have disclosed a marked discontinuity in the behavior of glass in the region of the softening point.

Ten years ago Twyman⁴ tested the application of Maxwell's⁵ equation for the disappearance of stress in a viscous body to

¹ TURNER: *J. Soc. Glass Tech.*, **9**, 147 (1925).

² MOREY and BOWEN: *J. Phys. Chem.*, **28**, 1167 (1924).

³ *J. Soc. Glass Tech.*, **9**, 226 (1925).

⁴ *J. Soc. Glass Tech.*, **1**, 61 (1917).

⁵ *Phil. Mag.*, [4] **35**, 133 (1868).

the problem of annealing glass. He determined the change of mobility (rate of change of strain with time under constant stress) with temperature and found the following formula to hold:

$$\frac{dS}{dt} = M = k \cdot 2^{\frac{\theta}{8}}$$

where M is the mobility, k a constant depending on the nature of the glass, and θ the temperature. English¹ confirmed this result with a large number of glasses of differing composition, except for the slight modification that the temperature interval was changed from 8 to 9°. This means that the mobility of a glass is either doubled or halved according to whether the temperature rises or falls by each 9°. In this connection attention should be called to Gray and Dobbie's² observation that the specific conductivity of a number of glasses was doubled for each 9° rise in temperature.

While these observations would seem to furnish quantitative evidence to support the view that the change of glass from a molten liquid to a rigid form is a continuous one, Tool and Valasek³ showed, as a matter of fact, that glass exhibits a marked discontinuity in behavior below the softening temperature. Above a "critical temperature" T_c , all glasses examined including a fused boric acid glass,⁴ exhibited a sudden increase in the rate of absorption of heat with rise of temperature, which was maintained up to a temperature T_s , slightly below the softening temperature. This is illustrated by the behavior of a borosilicate glass both on heating and on cooling as shown in Fig. 37. The heat effect at various temperatures was measured by the aid of a differential thermocouple.⁵ This is given in terms of galvanometer deflections which are plotted as abscissas against temperatures of the glass as ordinates. The range of temperatures,

¹ *J. Soc. Glass Tech.*, **7**, 25 (1923).

² *Proc. Roy. Soc. (London)* **63**, 38 (1898); **67**, 197 (1900).

³ *Bur. Standards, Sci. Papers*, **15**, 537 (1919-20).

⁴ In recent quantitative observations on a boric oxide glass SAMSOEN: [*Compt. rend.*, **181**, 354 (1925); SAMSOEN and MONVAL: **182**, 968 (1926)] found a region of heat absorption and a sharp rise in specific heat at a temperature of about 217°. This was followed by a twelvefold change in the coefficient of expansion at about 245°.

⁵ BURGESS and LECHATELIER: "Measurements of High Temperatures," 3rd. ed., 383 (1912); BURGESS: *Bur. Standards, Sci. Papers*, **5**, 199 (1908).

$T_c T_s$, was found to coincide with what is called the "annealing range" of temperature as indicated by a change in double refraction within which glass may be regarded as plastic. It appears, therefore, that heat of absorption and the rapid softening of glass are allied phenomena.

Following up the above observations, Peters and Cragoe¹ determined the thermal expansion of a number of glasses from 20° to the softening temperature. In all cases, the thermal

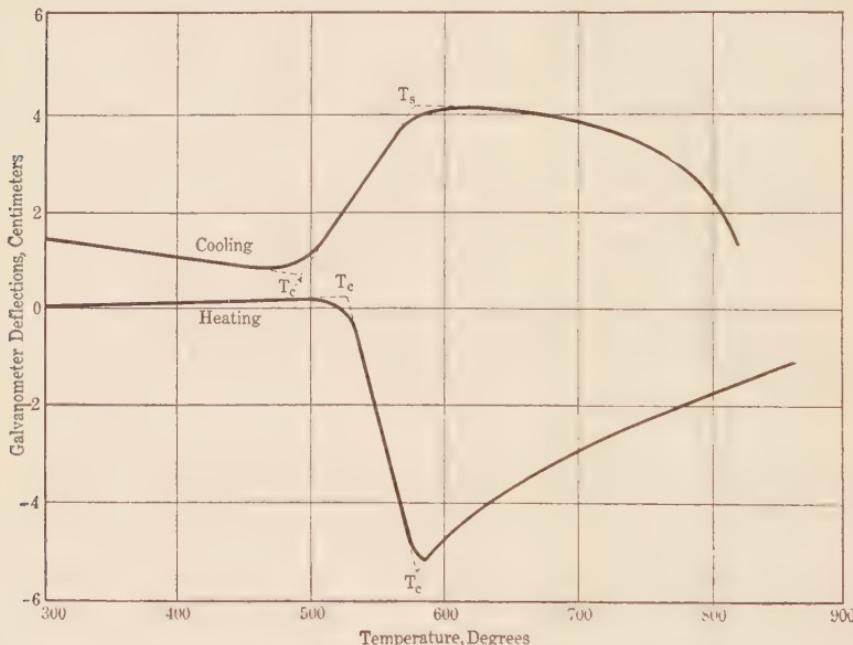


FIG. 37.—Heating and cooling curves for a borosilicate glass.

expansion remained constant up to very close to T_c , which was identical with the critical temperature for the glasses studied by Tool and Valasek. At T_c the coefficient of expansion underwent a sudden change of value, again becoming constant and remaining so over the greater part of the range $T_c T_s$; but the value over the latter range was from four to seven times as great as over the range 20° to T_c . The general results of Peters and Cragoe were confirmed by Turner with a series of soda-lime-silica glasses, by

¹ *J. Optical Soc. Am.* **4**, 105 (1920); *Bur. Standards, Sci. Papers*, **16**, 449 (1920).

Parks and Huffman¹ with a propylene glycol glass, and by Samsoen² with a glycerin glass. A typical curve for a soda-lime-silica glass is reproduced in Fig. 38 in which the linear coefficient of expansion is plotted against temperature.

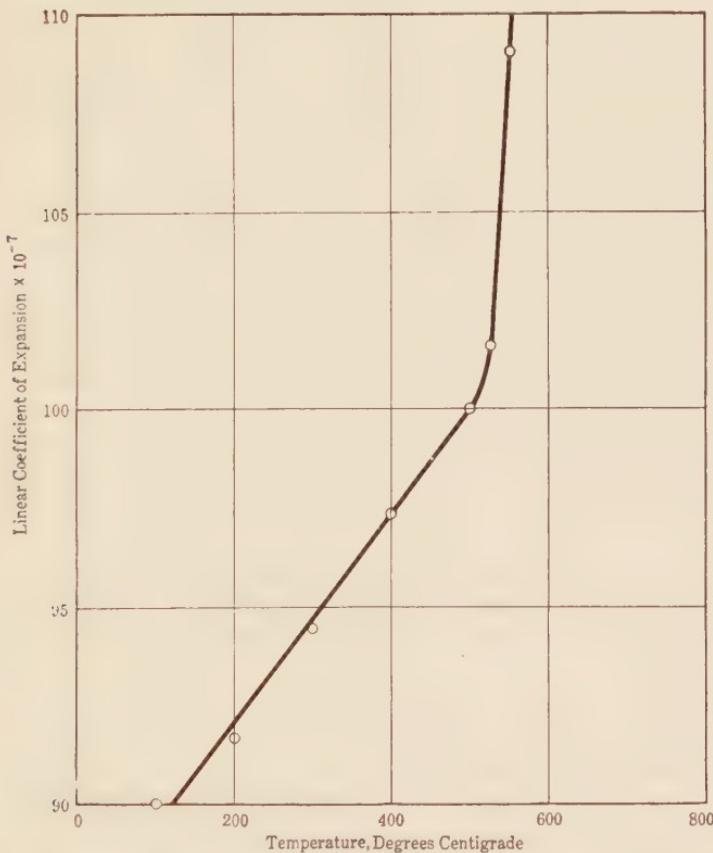


FIG. 38.—Variation of thermal coefficient of expansion of a soda-lime-silica glass with temperature.

Travers³ points out that a marked change in volume near the solidifying point furnishes the only way of accounting for the fact that when two soft glasses of different makes are sealed together, they join perfectly but show a ridge at the point of

¹ *J. Phys. Chem.*, **31**, 1842 (1927).

² *Compt. rend.*, **182**, 518 (1926).

³ "The Physics and Chemistry of Colloids and Their Bearing on Industrial Questions," 62 (1920).

union. This could not be caused by any difference in the rate of contraction over a range outside that at which the glass possesses mobility.

The evidences of discontinuity in the properties of glass in the neighborhood of the softening point is strongly supported by Griffith's¹ observation that below a certain temperature glass does not behave merely as a viscous liquid. This conclusion was reached from a study of the surface tension of an English glass with a relatively high softening temperature. In the neighborhood of 1100° the surface tension was measured by Quincke's drop method; but at lower temperatures, this was obviously impractical and the following procedure was used: Fibers of glass were prepared 2 inches long and from 0.002 to 0.001 inch in diameter with enlarged spherical ends. These fibers, supported horizontally in stout wire, were placed in an electric resistance furnace maintained at the desired temperature and suitable weights were hung on their midpoints, the enlarged ends preventing any sagging except that due to extension of the fibers. Viscous stretching of the fibers occurred under these conditions until the suspended weight was just balanced by the vertical component of the tension in the fibers. In the steady state, the latter was due entirely to the surface tension of the glass whose value was calculated from the observed sag in the fiber by means of the expression

$$\pi dS \sin \frac{1}{2}\theta = W$$

where d is the diameter of the fiber, S the surface tension, θ the angle of suspension between the two halves of the fiber, and W the suspended weight. This method was found to be applicable between 900 and 730°. Above 900 the viscosity was insufficient for an observation to be made before the fiber commenced to break up into globules. Below 720°, on the other hand, observations made on fibers of different diameters were inconsistent, the apparent surface tension being higher for the larger fibers. The meaning of this result is that below 730° the glass is not a perfect viscous liquid, as it is usually assumed to be, but exhibits a solid stress which increases from 0 at 730° to 1.3 pounds per square inch at 657° and 24 pounds per square inch at 540°.

¹ *Phil. Trans.,* **221 A**, 163 (1921).

More recently, Filon and Harris¹ investigated the optical properties of glass heated under pressure and found that a portion of the applied stress was not optically shown. The obvious conclusion from this observation was that glass cannot be a homogeneous liquid but must consist of at least two phases.

In the light of the evidence, it seems reasonable to conclude that glass is not a homogeneous liquid. An alternative hypothesis is that it is a colloid, exhibiting the properties of an elastic jelly in the rigid form and the properties of a sol in the molten state.² From this point of view the changes which glass undergo on cooling the melt may be likened, qualitatively at least, to the sol-gel transformation in such systems as gelatin-water.

The suggestion that glass is a colloid usually implying some form of a polyphase liquid system is not new. Thus Barus³ made use of this point of view 30 years ago to account for the behavior of glass toward water. At a pressure of 10 atmospheres and a temperature of 185°, he found glass to be transformed into an aqueous gel which possessed all the properties of a glass in the sense that it was compact and apparently homogeneous. On heating the gel, water was volatilized, leaving a porous whitish mass. It thus appears that glass is a jelly which can be swollen by water in much the same way as gelatin is, provided one works at a pressure sufficiently high to overcome the cohesion of the glass molecules.

Although the view that glass is a colloidal system resembling an elastic jelly is supported by considerable evidence, a great deal of work must be done before an adequate picture of the constitution and structure of the vitreous mass can be given. Quineke⁴ suggests that glass possesses a jelly-like structure built up of invisible foam walls separating foam cells, the walls and cells consisting of a series of liquid phases each containing several modifications of silicic acid. This view was reached from a careful examination of copper aventurine glass which contains microscopic crystals of copper in a transparent glass. He noted that

¹ Proc. Roy. Soc. (London) **103 A**, 561 (1923).

² Cf. TRAVERS: "The Physics and Chemistry of Colloids and Their Bearing on Industrial Questions," 63 (1920).

³ Am. J. Sci., [3] **41**, 110 (1891); [4] **6**, 270 (1898); **7**, 1 (1899).

⁴ Ann. Physik, [4] **46**, 1025 (1915).

in some cases the crystals develop in lines of similarly orientated octahedra while in other cases the crystals appear to be distributed over curved or plane surfaces. Quincke believes these observations to indicate the existence of a cellular or honeycomb structure in glass; but Quincke¹ considers all jellies to possess a honeycomb structure, whereas it seems probable that most, if not all, jellies have a filamentous or sponge structure.² In any case, Quincke's observations point quite as much to the presence of fibrils as of cell walls in glass. Sosman³ suggests that the solid character of silica glass is due primarily to the existence of long amorphous silica threads and their entanglements, and only secondarily to the interconnection of oxygen atoms. Bary⁴ regards glass at ordinary temperatures as a solid or semisolid solution of a crystalloid alkali silicate such as Na_2SiO_3 or K_2SiO_3 , in a condensed and highly polymerized colloidal silicate of a bivalent metal which may be formulated thus $[\text{CaO} = (\text{SiO}_2)_n = \text{CaO}]$. The rigidity of the glass at ordinary temperatures is attributed to the large size of the silicate molecules. Heating is believed to cut down the rigidity by depolymerization and decondensation of the hypothetical silicates. Plasticity which occurs above a certain temperature is attributed to the plasticizing effect of dissolved alkali silicate on the colloid.⁵ Bary admits that the hypothetical constitution of glass which he proposes may need modification in places, but points out that it enables one to give a reasonable interpretation of many phenomena unexplainable on the assumption that glass is simply a supercooled liquid.

DEVITRIFICATION

The tendency of certain constituents of glass to crystallize often leads to devitrification, a phenomenon in which relatively large crystals are formed in the glass, rendering it opaque and unworkable. Some glasses are very likely to devitrify during cooling

¹ Drude's *Ann.*, **9**, 793, 969 (1902); **10**, 478, 673 (1903).

² Cf. WEISER: "The Hydrous Oxides," 12 (1926).

³ *J. Franklin Inst.*, **194**, 741 (1922).

⁴ *Rev. gén. colloides*, **3**, 1, 46 (1925); cf., also, DOELTER: *Ibid.*, **2**, 162 (1924).

⁵ BARY: *Rev. gén. mat. plastiques*, **1**, 4 (1925); RUFF: *Z. anorg. Chem.*, **133**, 187 (1924).

while other glasses must be kept near the temperature of liquefaction for hours before visible crystals appear. All depends on the composition of the glass and the conditions of cooling. While many silicates may be cooled quite slowly without crystallizing, the fused silicates of calcium and magnesium form crystals if not quickly chilled, an accomplishment which is rather difficult since the compounds combine high thermal capacity with low thermal conductivity. The crystals formed during the devitrification of ordinary soda-lime-silica glass are probably calcium silicate chiefly, since this compound exhibits the greatest tendency to crystallize of any salt in the group. To obtain a good glass it is necessary, therefore, that the lime content should be kept within fairly well-defined limits.

Tammann¹ recognized three main factors which control the spontaneous crystallization of supercooled melts of one component: first, its ability to crystallize spontaneously as measured by the number of centers of crystallization formed in unit mass in unit time; second, the speed of crystallization; and third, the viscosity. The tendency to crystallize spontaneously and the speed of crystallization first increase with diminishing temperature and then decrease again, while the viscosity increases steadily. Alexander² points out that in mixtures a fourth factor, mutual protection, may be of outstanding importance. Every substance in forming microscopic crystals must necessarily pass through the colloidal zone where surface forces such as adsorption may exercise a dominant influence. The mutual adsorption of various silicates will introduce a time lag in the crystallization process which is cumulative and is enhanced by the increasing viscosity of the mass. For example, the presence of alumina and titania³ in glass is inimical to devitrification although it is very difficult to cool sillimanite, $\text{Al}_2\text{O}_3\text{SiO}_2$, alone sufficiently rapidly to prevent crystallization.

RUBY GLASS AND RELATED PRODUCTS

Many transparent colored glasses owe their color to the presence of colloidally dispersed substances. An important example

¹ *Z. Elektrochem.*, **10**, 532 (1904).

² "Colloid Chemistry," 2nd ed., 137 (1924).

³ TURNER and SHEEN: *Pottery Gaz.*, **48**, 1804 (1923).

of this class of bodies is ruby glass obtained by melting a suitable glass with gold, copper, selenium, or with compounds of these elements.

Gold ruby glass is readily prepared by melting a lead or barium glass and adding gold as gold chloride¹ or in the form of purple of Cassius as used by Kunkel, the discoverer of the glass. If the glass is cooled quickly it usually remains colorless, but if cooled slowly or reheated to a temperature well below the melting point, it becomes colored owing to the separation of a very large number of particles of colloidal gold of the size to transmit red light. If the temperature is too high or the time of heating too long, the red color may change to a violet and then to a blue owing to increase in the size of the particles. These changes in color are exactly the same as are observed in gold hydrosols and for the same reason. If stannic oxide is added to the glass it protects the gold so that there is less tendency for the material to turn blue on prolonged warming.²

While the cause of the red to blue color of gold ruby glass is understood, it is not obvious why the chilled melt is colorless at first. Zsigmondy³ points out that this cannot be due to the formation of a colorless gold salt⁴ since the mass is colorless, even in the presence of strong reducing agents. He concludes, therefore, that the colorless glass consists of a supersaturated solution of metallic gold in the vitreous mass, together with gold nuclei which arise from the supersaturated solution on cooling and grow, during the subsequent heating, into particles of the size to transmit red light. Zsigmondy offers no adequate reason for assuming that most of the gold is in true solution and from analogy with colloidal solutions of the alkali metals⁵ one would expect a solution of gold to have the color of gold vapor. On the other hand, this is not necessarily true, since metals cathodically disintegrated and atomically dispersed in a suitable salt layer do not color it.⁶

¹ SIEDENTOPF and ZSIGMONDY: *Drude's Ann.*, [4] **10**, 1 (1903); ZSIGMONDY-ALEXANDER: "Colloids and the Ultramicroscope," 168 (1909).

² BELLAMY: *J. Am. Ceram. Soc.*, **2**, 313 (1919).

³ "Colloids and the Ultramicroscope," 168 (1909).

⁴ Cf., however, SILVERMAN: *J. Am. Ceram. Soc.*, **7**, 796 (1924).

⁵ SVEDBERG: *Ber.*, **39**, 1705 (1906).

⁶ WEBER and OOSTERHUIS: *Koninkl. akad. Witensch. Amsterdam*, **25**, 606 (1916).

The possibility that all the gold in the colorless glass is colloidally dispersed, the particles being too small to affect the beam of light, must not be overlooked, since Zsigmondy is willing to admit that a part of it is in such a state. Moreover, von Weimarn¹ points out that in natural gold-bearing quartz, the gold may appear in colorless dispersion.

The amount of gold involved in ruby glass is quite small, 0.01 per cent giving a pink color and 0.1 per cent a bright red. There are some billions of gold particles per cubic centimeter, the weight of the particles being of the order of 10^{-15} grain and their diameter from 4 to $30\mu\mu$.

Copper is used instead of gold in the manufacture of a cheaper form of ruby glass. Copper either as oxide or metal always gives green to greenish blue tints when added to glass in the ordinary way. When the oxidation of the element is prevented by the presence of a reducing agent and the glass is cooled slowly or subjected to repeated heating followed by cooling, an intense ruby color is produced. Glasses with particles of quite different sizes are recognized technically. In the true ruby glass the particles are of ultramicroscopic dimensions; in the opaque copper-red haematinon, they are microscopically visible; and in aventurine glass they exist as spangles visible to the naked eye. From analogy with gold ruby glass one would expect the color of the copper glass to be due to colloidal copper. This view is held by Williams,² but Seger³ attributes the color to cuprous oxide or cuprous silicate. This opinion is shared by Stokes⁴ since he believes that finely divided colloidal copper is blue, whereas it is the coarser particles which are blue. Zulkowski⁵ believes that cuprous oxide is responsible for the color. Bancroft⁶ points out that we may have metallic copper in one glass and cuprous oxide in another. This is a safe position to take so long as there is no way of distinguishing between the two cases. It should be possible, however, to distinguish a copper or cuprous oxide glass

¹ *Kolloid-Z.*, **11**, 287 (1912).

² *Trans. Am. Ceram. Soc.*, **16**, 284 (1914).

³ "Collected Writings," **2**, 734 (1902).

⁴ "Mathematical and Physical Papers," **4**, 245 (1904).

⁵ *J. Soc. Chem. Ind.*, **16**, 441 (1897).

⁶ *J. Phys. Chem.*, **23**, 615 (1919).

from one containing copper silicate since the former should scatter light, whereas the latter should be optically empty.

Selenium imparts a red to pink color to moderately alkaline glasses, the color being a purer red with potash than with soda glasses. The tint is that of the colloidally dispersed element which gives a hydrosol the color of arterial blood.¹ In strongly alkaline melts, selenium gives a chestnut brown color and the glass is optically empty.² Tellurium colors glass coral to purple-red in low concentrations and a steel blue in higher concentrations. Sulfur imparts a yellow to yellowish-brown color to glass containing no heavy metals; this is probably due to polysulfides since the glasses are reported to be optically empty.³ Addition of sulfur to calcium glasses yields a blue color which is apparently due to colloidal sulfur. Wolfgang Ostwald⁴ prepared blue and green sols of colloidal sulfur by introducing the element into molten sodium chloride, borax bead, liquid ammonia, and hot organic liquids such as glycerin. He considers, furthermore, that the blue color of ultramarine is due to colloidal sulfur.⁵ In this connection, it is interesting to note that the mixture of sulfur, silicates, and other salts when melted together yields yellowish "mother of ultramarine" which, like colorless gold ruby glass, is only transferred into the commercial product by careful reheating.

The addition of silver to glass as a surface stain yields the beautiful yellow color⁶ which characterizes a silver hydrosol having the finest particles. For enamels, silver is added to the mass of the glaze and not as a surface stain. A yellow stain of silver on a cobalt blue enamel gives a green. Baneroff⁷ points out that this is the ceramic analogue of the green tree frog which has no green pigment whatsoever but whose green color is due to a structural blue overlaid with a yellow pigment.

¹ SCHULZE: *J. prakt. Chem.*, [2] **32**, 390 (1885).

² FENAROLI: *Kolloid-Z.*, **16**, 53 (1915).

³ FENAROLI: *Kolloid-Z.*, **16**, 53 (1915).

⁴ *Kolloidchem. Beihefte*, **2**, 449 (1911); LANGE: "Die Schwefelfarbstoffe, ihre Herstellung und Verwendung," (1912); cf. *Kolloid-Z.*, **12**, 61 (1913); OSTWALD and AUERBACH: *Kolloid-Z.*, **38**, 336 (1926).

⁵ Cf. MORGAN: *J. Oil and Color Chemists' Assoc.*, **2**, 120 (1919); KEME: *Chem. Ztg.*, **47**, 513 (1923).

⁶ ROSENHAIN: "Glass Manufacture," 185 (1908).

⁷ "Applied Colloid Chemistry," 201 (1921).

The coloration of glass by oxides is probably due, in many cases, to the colloidally dispersed pigments. Thus the amethyst to violet color which manganese imparts to glass is due to some oxide although people do not agree as to whether the color results from Mn_2O_3 ,¹ MnO_2 ,² or Mn_3O_4 .³ It is possible that one or all of these oxides may be present in different glasses but the known wide variation in color of manganese dioxide from very finely divided red particles⁴ to coarser black particles, makes it seem probable that the dioxide is responsible for the color. The hydrosol of manganese dioxide is usually a clear brown but a red hydrosol has been prepared.⁵ The blue color of cobalt glass is probably due to very highly dispersed cobalt oxide.⁶ Larger particles of this oxide are red rather than blue. The color of the ruby is due to a red modification of chromic oxide.⁷

The base of enamels is generally a colorless glass in which is suspended particles of an opaque metallic oxide or salt. The dispersed phase is usually stannic oxide but titania, zirconia, arsenic trioxide, calcium phosphate, cryolite, and fluorspar have been substituted for stannic oxide. All of the compounds are colorless and their addition renders glass opaque owing to the difference in refractive index. Thus, natural stannic oxide has a much higher refractive index for yellow light than glass has. The addition of antimony oxide to a lead glass gives an opaque yellow product, the second phase being lead antimonate, sometimes called Naples yellow.

Iron compounds usually color glass green or yellow but black, blue, brown, and red glazes have been obtained. The green may be due to dissolved ferrous compounds and the yellow, brown, and red to ferric oxide of varying degrees of subdivision.⁸ The black is probably due to relatively coarsely dispersed ferro-ferric oxide and the blue may be due to more finely divided

¹ SCHOLES: *J. Ind. Eng. Chem.*, **7**, 1037 (1915); *J. Soc. Chem. Ind.*, **35**, 116 (1916); *Am. Mineral.*, **9**, (1924).

² ROSCOE and SCHORLEMMER: "Treatise on Chemistry," **2**, 608 (1923).

³ SILLIMAN: "Elements of Chemistry," **2**, 175, 180 (1831).

⁴ VAN BEMMELEN: *J. prakt. Chem.*, [2] **23**, 324, 379 (1881); FREMY: *Compt. rend.*, **82**, 475, 1231 (1876).

⁵ RIDEAL and NORRISH: *Proc. Roy. Soc. (London)* **103 A**, 365 (1923).

⁶ WEISER: "The Hydrous Oxides," 149 (1926).

⁷ STILLWELL: *J. Phys. Chem.*, **30**, 1441 (1926).

⁸ Cf. WEISER: "The Hydrous Oxides," **70** (1926).

magnetite or a blue modification of the compound analogous to the red modification of chromic oxide.¹ Foster² attributes the black color of Greek and Roman pottery to ferrous iron probably as ferrous silicate. Franchet,³ however, reproduced the black luster simply by grinding equal amounts of magnetite and a frit prepared by fusing 55 parts of quartz sand with 45 parts of sodium carbonate at 850°. The opacity of the enamel was due to the presence of more magnetite than will dissolve in the flux.

Opalescence in certain glasses is produced by the introduction of suitable amounts of arsenic trioxide, stannic oxide, calcium phosphate, cryolite, or mixtures of aluminum- and fluorine-bearing compounds. The phenomenon results from the presence of highly dispersed particles in the glass. Silverman⁴ attributes the opalescence of aluminum-bearing glasses free from alkali chlorides or sulfates to the presence of finely divided, positively charged particles of colloidal alumina. The addition of chlorides or sulfates to the fused melt causes agglomeration of the particles, producing alabaster glasses in which opalescence is no longer visible, the glasses transmitting white light instead of firey light.

¹ BANCROFT: *J. Phys. Chem.*, **23**, 625 (1919); "Applied Colloid Chemistry," 2nd. ed., 438 (1926).

² *J. Am. Chem. Soc.*, **32**, 1259 (1910).

³ *Compt. rend.*, **152** 1097 (1911).

⁴ *J. Am. Ceram. Soc.*, **1**, 247 (1918); **7**, 796 (1924).

CHAPTER XXI

CLAY

The term "clay" is usually defined as a soft or consolidated rock consisting essentially of hydrous silicates of alumina, the chief characteristics of which are plasticity when wet and the property of baking to a hard stone-like mass when heated to redness. In view of the fact that there is some doubt as to the manner in which the alumina and silica are combined, Searle¹ prefers to regard clay as "a naturally occurring earthy material whose chief characteristic is its plasticity and whose essential constituents are reported in an analysis of the substance to be alumina, silica, and water." This latter definition is sufficiently broad to include pure china clays whose composition may approach that of the crystalline mineral kaolinite and the highly siliceous and plastic material commonly referred to as brick clays which are known to contain as much as 60 per cent of material of a sandy non-plastic nature.

ORIGIN AND COMPOSITION OF CLAYS

Clays are secondary products formed, as a rule, by the weathering of feldspar and feldspathic minerals. Two general classes are recognized: residual clays and sedimentary clays. The first class is usually found overlying or adjacent to the parent rock. The mineral character varies from the finer and purer product nearer the surface to the mixture of clay and undecomposed rock with which it is in contact. It seems probable that the weathering consists primarily in the slow hydrolytic action of water on the feldspathic rock.² The action of carbonic acid,³ hydrogen sul-

¹ "Brit. Assoen. Advancement Sci., Third Rept. on Colloid Chem.," 114 (1920).

² CAMERON and BELL: *Bull. U. S. Bureau of Soils*, **30**, 16 (1905).

³ Cf. ROSE: *Pogg. Ann.*, **55**, 415 (1842); **82**, 545 (1851); **94**, 481 (1855); STREMME: *Z. prakt. Geol.*, **16**, 122, 443 (1908); **17**, 353, 529 (1909); **18**, 161, 389 (1910); **19**, 329 (1911); STAHL: *Ibid.*, **19**, 163 (1911); BAYLEY: *Econ. Geol.*, **15**, 235 (1920).

fide, and organic acids such as humic may, likewise, have a kaolinizing action on the feldspar.¹ Residual clays usually contain a smaller amount of iron and organic matter than sedimentary clays and are therefore lighter in color.

Sedimentary clays are formed by the transportation in water and redeposition of residual clays; hence they may have no direct relationship with the rock with which they are in contact. Since all kinds of debris from the rock and soil over which the clays are carried may be transported with the clay, the sedimentary deposits are usually less pure than the residual clays.

In view of the manner in which clays are formed and laid down, it is not surprising to find a wide variation in the composition of different deposits. Among the classes of clay which are important in the manufacture of ceramic material are china clay, ball clay, and fire clay. Many other classes are recognized in the ceramic industry,² but these three will serve to illustrate the variation in composition, properties, and uses of clays.

It is generally believed that the mineral feldspar is one of the most important sources of clay. The weathering of pure crystalline orthoclase $KAlSi_3O_8$ apparently gives $Al_2O_3 \cdot SiO_2 \cdot 2H_2O$. This is the formula of the mineral kaolinite and a clay which approaches this composition is called kaolin. This term is said to be a corruption of the Chinese *kao*, high, and *ling*, hill, in allusion to the Kaoling mountain, North China, from which the Chinese obtained clay for the manufacture of porcelain. It corresponds to the English term china clay, so-called because of its use in the fabrication of "china" or porcelain ware. These terms are now applied to all the purer residual clays which analyze 33 to 40 per cent alumina, 45 to 60 per cent silica, and 11 to 14 per cent water, together with very small percentages of such impurities as Fe_2O_3 , Na_2O , K_2O , CaO , and MgO .

The name ball clay is applied to certain sedimentary clays which possess high plasticity and tensile strength in the moist condition and which burn to a whitish or light-buff color. The chief use of this type of clay is in the manufacture of white

¹ WÜST: *Z. prakt. Geol.*, **15**, 19 (1907); SMIRNOV: "The Influence of Humus Compounds on the Weathering of Aluminosilicates," Khrakow (1915).

² Cf. RIES: "Clays," 23-28 (1914).

earthenware. Ball clay is generally finer in grain than china clay, and contains more silica as well as more organic matter and other impurities. The firing temperature is considerably lower than that of china clay.

Fire clay is the term applied to clay which fuses above 1500°. While this would include many of the purer residual clays, the term has been restricted in use to certain shales, usually underlying coal seams which have a high fusion point and are employed largely in the manufacture of firebricks, furnace linings, glass pots, and other articles which may be subjected to a high temperature.

The composition of some typical clays is given in Table L. It is obvious that clays having similar composition, reported as

TABLE L.—COMPOSITION OF TYPICAL CLAYS¹

Clay source	Kaolin-ite	Kaolin, Webster, N. C.	Ball clay, Edgar, Fla.	Fire clay, St. Louis, Mo.	Brick clay (1), Harrisburg, Tex.	Brick clay (2), Harrisburg, Tex.
SiO ₂	46.3	45.70	56.11	57.62	80.39	80.84
Al ₂ O ₃	39.8	40.61	39.55	24.00	9.82	8.09
Fe ₂ O ₃	1.39	0.35	3.30	2.88	2.25
MgO.....	0.09	0.13	0.30	0.45	0.26
CuO.....	0.45	0.70	0.42	1.44
K ₂ O.....	2.82	0.50	Trace	Trace
Na ₂ O.....	0.20	0.19	0.10
TeO ₂	1.20	0.35	0.78
H ₂ O.....	13.9	9.33	13.78	13.20	3.11	6.00
Plasticity...	Low	Low	Very high	High	Fair	High

¹ Compiled from RIES: "Clays" (1914).

the oxides, may exhibit widely different properties. Thus the slightly plastic kaolin from Webster, N. C., differs but little in composition from the highly plastic ball clay from Edgar, Fla. This is further illustrated in a striking way by the two clays obtained from different beds in the same bank near Harrisburg, Tex. The first is fairly plastic, requires 18.7 per cent of its weight of water for mixing, shrinks 4.8 per cent on drying, without cracking, and has an average tensile strength of 188 pounds per

square inch. The second sample is highly plastic, requires 19.8 per cent water for mixing, shrinks 8.6 per cent on drying with the formation of cracks, and has an average tensile strength of 275 pounds per square inch. These examples, which are not exceptions, show that the ultimate analyses of a clay gives little information concerning those physical characteristics which are of fundamental importance in the ceramic industry.

THE CONSTITUTION OF CLAY

The definite crystalline compound kaolinite is sometimes found in clays but its presence is the exception and not the rule. Microscopic examination usually reveals the clayey matter as an amorphous flocculent aggregate associated with grains of other mineral matter such as quartz, feldspar, muscovite, calcite, rutile, gypsum, etc. If a commercial sample of clay is shaken with water, allowed to stand for a few minutes, and poured through a fine-mesh sieve, the process being repeated a number of times with fresh water, the residue will not be plastic, as a rule, but will resemble sand, or a mixture of gravel, sand, and rock powder. Analysis of the finest particles obtained by repeated sedimentation or careful elutriation sometimes shows the composition to be approximately $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$, identical with kaolinite. This is true for many kaolins and certain clays such as the Cornish clays; but many highly plastic clays and fireclays yield a product considerably richer in silica and deficient in the elements of water. The constancy of composition of the finest particles from purer china clays has led to the conclusion that all clays contain an essential substance corresponding to kaolinite but differing from the latter in being hydrous and amorphous. This material has been called "clay substance,"¹ "true clay,"² and "clayite"³ by different investigators. So frequently has this substance been referred to that its existence is taken for granted by many people. Ries,⁴ however, emphasizes the fact that the term clay refers to a

¹ SENFT: "Die Steinschutt und Erdboden," Berlin, 236 (1867); SEGER: "Collected Writings," I, 46 (1902).

² BRONGNIART and MALAGUTI: *Arch. Muscum Hist. Natl.*, **1**, 234 (1840); **2**, 271 (1841).

³ MELLOR: "Inorganic and Theoretical Chemistry," London, **6**, 467 (1925).

⁴ "Clays," 8 (1914).

physical condition rather than to a definite composition and Searle¹ points out that "true clay" has never been isolated, both the composition and properties of the elutriated product differing with the origin and nature of the parent clay.

Since the term clay connotes a physical condition rather than a definite chemical composition, the question arises as to the cause of the distinctive physical properties of clay, most important of which is plasticity. The answer is that clays owe their distinctive characteristics to the presence in them of colloidal matter, first recognized by Schlösing² in 1872. We thus reach the conclusion that clays are essentially mixtures of non-clayey, adventitious minerals such as sand with varying amounts of colloidal material. Since the amount of the latter which can be separated from clays is relatively small, it seems probable that the coarser non-plastic particles are covered with a film of the colloidal matter which becomes gelatinous when wet. It is still undetermined whether the colloidal matter is essentially the hydrous oxides of silica and alumina or whether it is an intermediate composition, a hydrous aluminum silicate. Searle³ suggests that the colloidal matter of some clays may be hydrous silicates and of others the hydrous oxides. Thus, the composition of the elutriated product from certain of the purer china clays indicates that the colloidal matter may be a hydrous aluminum silicate. On the other hand, colloidal matter from the lateritic clays, which are characterized by a large proportion of alumina and silicate soluble in hydrochloric acid, may be merely mixtures of the two hydrous oxides. This view is supported by the variability in composition of the elutriated product and by the similarity of the clayey matter to a mixture of alumina and silica.

At the present time, nobody knows in what respect an amorphous hydrous aluminum silicate will differ from an amorphous mixture of the hydrous oxides in the same proportion. Until we do know, it is simply a guess as to whether the colloidal matter of a given clay is chiefly the former or chiefly the latter. It is

¹ "Brit. Assocn. Advancement Sci., Third Rept. on Colloid Chem.," 115 (1920).

² *Compt. rend.*, **79**, 376, 473 (1874); cf., also, ROHLAND: *Z. anorg. Chem.*, **31**, 158 (1902); VAN DER BELLEN: *Chem. Ztg.*, **27**, 433 (1903).

³ "Brit. Assocn. Advancement Sci., Third Rept. on Colloid Chem.," 116 (1920).

quite likely, however, that the first product of the weathering of feldspar is a definite hydrous aluminum silicate. Some observations on the synthesis of aluminum silicate bear on this question:

Schwarz and Brenner¹ mixed solutions of specially prepared sodium silicate and aluminum chloride, filtered off the precipitates which were dried on the water bath, pulverized with an agate mortar, and subsequently washed with water, alcohol, and ether. In the first series of experiments the molar ratio $\text{AlCl}_3:\text{Na}_2\text{SiO}_3$ was kept constant at 2:3, the concentrations of the solutions being varied. It was found that the ratio of alumina to silica in the precipitates increased with the dilution but it was always slightly less than the ratio 1:1.5. In the second series of experiments, the molar proportions mixed were varied from $2\text{AlCl}_3:1.5\text{Na}_2\text{SiO}_3$ to $2\text{AlCl}_3:10\text{Na}_2\text{SiO}_3$, and the mixtures allowed to stand 4 hours. The proportion of silica in the precipitate was found to increase with increasing concentration of sodium silicate up to 6 molar proportions of SiO_2 ; but the latter never entered quantitatively into the reaction. When 6 to 10 molar proportions of silica were present, the ratio of $\text{Al}_2\text{O}_3:\text{SiO}_2$ was invariably 1:2, a composition that was unaffected by the presence of an excess of silica. These observations should be repeated with different sets of solutions in order to determine whether the ratio represents a compound or the limiting adsorption for the solutions used. In a third series of experiments, the molar ratio was kept constant at $2\text{AlCl}_3:3\text{Na}_2\text{SiO}_3$ and the precipitate was kept in contact with the mother liquor for varying times from 15 minutes to 18, 34, 2, and 21 days. The initial product was found to be a hydrous gel which approached the composition $\text{Al}_2\text{O}_3 \cdot 1.5\text{SiO}_2$. This took up SiO_2 from the mother liquor and in the course of approximately 200 hours, had gone over to $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, this composition being maintained indefinitely. When dried at 110° it analyzed for $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ corresponding to kaolinite. Analysis by x-rays was made of precipitates 2 days old, 8 days old, and 3 weeks old. The first two were found to be amorphous, whereas the third was crystalline. The primary amorphous gel had, in the course of time, gone over into a crystalline compound $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ which appears to be similar or closely related to natural kaolinite.

¹ *Ber.*, **56 B**, 1433 (1923).

The synthetic product differed from an amorphous kaolin of the composition $\text{Al}_2\text{O}_3 \cdot 2.77\text{SiO}_2 \cdot 2.07\text{H}_2\text{O}$ in that the former lost 1 molar proportion of water below 260° and the second proportion between 360 and 640° , whereas the latter was found to lose its 2 molar proportions of water continuously above 360° , becoming anhydrous at 640° . The greater tenacity with which the natural kaolin holds on to its first molecule of water may be due to a difference in physical and molecular structure brought about by prolonged ageing. It is unfortunate that Schwarz and Brenner did not carry their observations to the point of establishing definitely whether or not their synthetic crystalline $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot 2\text{H}_2\text{O}$ was identical in crystal structure with natural kaolinite.

From the above observations, it would appear that in the neutral ternary system $\text{Al}_2\text{O}_3\text{—SiO}_2\text{—H}_2\text{O}$, a single compound $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot x\text{H}_2\text{O}$ is capable of formation and its formation is uninfluenced by the presence of an excess of silica or by the duration of the reaction. This compound is formed with particular readiness when 1 mole of Al_2O_3 is in contact with at least 6 mols of SiO_2 as is the case in feldspar. It seems reasonable to conclude, therefore, that the first product of the weathering of feldspar is the hydrous aluminum silicate, $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot x\text{H}_2\text{O}$. This is formed in the presence of silica and other salts which may inhibit crystallization to a greater or lesser degree so that crystalline kaolinite is absent from most clays. It is probable that hydrous aluminum silicate undergoes hydrolysis to a certain extent with the formation of gels of the hydrous oxides.

PROPERTIES OF CLAYS

Plasticity.—Plasticity may be defined as the property of a material which enables it to change its shape without cracking when subjected to pressure, the new shape being retained when the deforming stress is removed.

A¹ mobile liquid is not plastic because it will not retain its shape. With increasing viscosity, a liquid or a suspension passes through the point of zero fluidity and there is a change, as Bingham has shown, from viscous to plastic flow. Molasses candy is plastic until it crystallizes. Glass becomes plastic when heated to a suitable temperature. These are cases of plastic liquids. Crystalline solids may become plastic under

¹ BANCROFT and JENKS: *J. Phys. Chem.*, **29**, 1215 (1925).

suitable conditions. Metals are squirted into rods or pipes because they are plastic under high pressures. The flow of a glacier is due, at least in part, to the plasticity developed in ice under high pressures.

Between the extreme cases of a solid such as a metal and a liquid such as glass or molasses candy, we have the intermediate case of putty, which is a mixture of whiting and oil, a solid with a liquid film around it. If a liquid is adsorbed strongly by a solid, thin films of the liquid will hold the solid particles together, while still permitting them to move relatively to one another. The tendency of the liquid surfaces to coalesce causes any break to heal at once. A liquid film will therefore act as a bond for solids and may make the mass plastic. One kind of oil is used as a binder in roads, and another to make putty out of calcium carbonate. Everybody knows that dry sand cannot be molded whereas wet sand can.

In the clay industry the term plasticity connotes not only that the clay can be molded under pressure but that it will harden on the application of heat, forming a rock-like mass. From this point of view wet sand alone is not plastic but requires the presence of some binding material of a gelatinous character. In clays, this gelatinous binding agent is apparently a film of colloidal aluminum silicate or of the hydrous oxides of silicon and aluminum on the surface of larger particles. The only difficulty with the simple hypothesis that the gelatinous material consists of the hydrous oxides of silicon and aluminum is the fact that the pure oxides do not take up water to form a gel after having been thoroughly dried out. Bancroft¹ suggested that the presence of some salt may account for the reversibility of the colloidal material on repeated moistening and drying. In accord with this view, it was found² that the addition of small amounts of sodium chloride plus traces of lithium chloride will make a kaolin plastic. This is not Nature's way, however, since there appears to be no connection between the lithium content of a clay and its plasticity. Moreover, lithium chloride tends to keep alumina gelatinous and the lateritic or alumina-rich clays are said not to possess high plasticity as a rule.

Following up the action of lithium chloride in rendering kaolin plastic, Jenks³ has succeeded in working out the mechanism of

¹ "Applied Colloid Chemistry," 160 (1920).

² BANCROFT and JENKS: *J. Phys. Chem.*, **29**, 1215 (1925).

³ Dissertation, Cornell University (1927).

the action of electrolytes in forming and preserving the plasticity of clays. The material that is capable of becoming gelatinous when moistened was found to be produced and maintained in the necessary physical condition by a simultaneous peptizing and flocculating action under changing conditions. It is known that alkalies and alkali carbonates have a peptizing action on clays and that salts, especially those with multivalent cations, tend to flocculate clays. Hence suitable mixtures of the two types of reagents exert a plasticizing effect on kaolin or the hydrous oxides of silicon and aluminum that is more pronounced than either alone. This is illustrated by some observations recorded in Table LI. A salt was added to a clay slip that had been made alkaline by the addition of an alkaline hydroxide or carbonate. The slip was evaporated to dryness on a water bath, the clay remoistened and molded into a testball. The air-dried testball was allowed to disintegrate under water and the time of disintegration recorded as the plasticity of the clay. It will be seen

TABLE LI.—EFFECT OF ELECTROLYTES ON THE PLASTICITY OF A KAOLIN

Electrolyte added	Na ₂ O equivalent, per cent	Plasticity
None	4.5
0.25 per cent NaCl.....	0.14	6.5
0.2 per cent Na ₂ CO ₃	0.12	15.0
0.1 per cent NaCl + 0.5 per cent Na ₂ CO ₃	0.67	12.0
0.8 per cent NaOH.....	0.60	8.0
0.4 per cent NaCl + 0.8 per cent NaOH.....	0.80	13.0
0.1 per cent LiCl.....	0.073	10.0
0.2 per cent Li ₂ CO ₃	0.17	11.0

that sodium carbonate is twice as effective as sodium chloride in increasing the plasticity and that the added effect due to the carbonate may be duplicated by allowing the chloride to react in an alkaline solution. Also, the deflocculating action of the dilute solution of sodium hydroxide alone and the later flocculating action of the concentrated solution obtained by evaporating off the water on the water bath did not increase the plasticity as much as a mixture of sodium hydroxide with the more powerful flocculating agent sodium chloride.

Silica was rendered plastic by treating with a solution of potassium hydroxide and barium chloride but not sodium chloride, followed by repeated air drying and moistening to plasticity. Plastic alumina was formed in a similar way by the simultaneous action of alkali chloride and hydroxide. This action is not specific since barium chloride and sodium sulfate can be substituted for sodium chloride, and sodium carbonate for sodium hydroxide.

If the gelatinous character of a clay results from ageing in the presence of both peptizing and flocculating agents, it follows that a non-plastic clay is one which contains but little salts or which has not developed plasticity because of too uniform conditions. The "rotting" of dug clay which increases its plasticity is probably due to the moisture and temperature variations which increase the amount of gelatinous material.

Since a gelatinous body consists of very finely divided particles that have adsorbed water strongly, it follows that a mixture of hydrous oxides or a hydrous aluminum silicate will continue to impart plasticity to a mass, even after drying repeatedly, provided the primary particles are prevented from coalescing or from agglomerating into dense aggregates. As already noted, such coalescence or agglomeration is inhibited by a suitable peptizing agent. One would expect a protective colloid to exert a similar influence. Since humus doubtless possesses the properties both of a peptizing agent¹ and a protective colloid, it is probable that it plays an important role in the development and maintenance of plasticity in many clays.² Ries³ showed that the addition of a 1 per cent solution of tannin to a clay noticeably increased the plasticity and at the same time deflocculated or peptized the larger aggregates. In addition, the tensile strength of the clay was doubled by this treatment. Acheson⁴ increased the plasticity of clays by adding tannin and alkalies until the hydrous mass was completely deflocculated, after which sufficient acid was added to coagulate the colloids to a pasty mass. Everyone knows how Pharaoh increased the burdens of the Israelites by

¹ See p. 364.

² Cf. KEPPELLER: *Chem. Ztg.*, **36**, 884 (1912).

³ *Trans. Am. Ceram. Soc.*, **6**, 44 (1904).

⁴ *Trans. Am. Ceram. Soc.*, **6**, 31 (1904).

withholding from them the straw which they used in making bricks. It is probable that the straw served as a source of tannin rather than as a binding material and that the burden imposed consisted in their having to make bricks with less plastic material.

Since the important thing for plasticity is relatively coarse particles coated with a film of colloidal matter which adsorbs water strongly, it should be possible to increase the plasticity by grinding. It is very difficult indeed to grind particles to ultramicroscopic dimensions; nevertheless, the plasticity of certain clays both soft and hard has been increased appreciably by prolonged grinding.¹ Johnson and Blake² claim to have made a non-plastic china clay plastic by this means; but they attributed this to the flattening out of the particles rather than to disintegration.

Since the bulk of the gelatinous material in clays is doubtless hydrous alumina and hydrous silica or an intermediate composition, it is natural to inquire what will be the effect of addition of these substances to a slightly plastic clay. Cushman³ found that when colloidal silica was added to such a clay, the air shrinkage and the tensile strength were increased but not the plasticity; with colloidal alumina, neither the air shrinkage nor the tensile strength was changed but the plasticity was increased; and with a mixture of the two hydrous oxides, both the binding power and the plasticity were augmented. Grout⁴ repeated these experiments but with negative results. The experiments should be carried out once more, taking precautions to see that the hydrous oxides are deposited in the colloidal state on the surface of the particles of the non-clayey material. For unless the hydrous oxides form a coherent gelatinous film on the non-clayey matter, their addition in small amounts can affect the plasticity but little.

People who do not regard the presence of suitable colloidal matter as a sufficient criterion for the plasticity of clays, as the ceramist uses the term, usually attribute the phenomenon to some purely chemical characteristics of the molecules of a clay.

¹ SEARLE: "Brit. Assocn. Advancement Sci., Third Rept. on Colloid Chem.," 131 (1920); WALKER: *J. Am. Ceram. Soc.*, **10**, 449 (1927).

² *Am. J. Sci.*, [2] **43**, 351 (1867).

³ *Trans. Am. Ceram. Soc.*, **6**, 7 (1904).

⁴ Cf. RIES: "Clays," 127 (1914).

substance,¹ or to plate-like structures of the particles.² As we have pointed out, the evidence for the existence of a true clay is lacking; and there appears to be no justification for attributing plasticity solely to the plate-like or lamellar structure of the particles. While the shape of the particles may influence the plasticity of a clay, there is little doubt that a clayey mass entirely free from gelatinous colloidal matter will be plastic only as wet sand is plastic and, like the latter, will not burn to a coherent mass.

Adsorption.—Adsorption by clays is so clearly related to their colloid content, that methods of determining the latter are based on the adsorption capacity of the clay for water, malachite green, and ammonia. Gile³ and his coworkers attribute 95 per cent of the adsorption capacity of a soil to its colloidal material and only 5 per cent to the non-colloidal matter. The total water-holding capacity of a clay will be influenced also by the mode of packing of the non-colloidal material but this factor is probably of lesser importance. Bouyoucos⁴ showed that some highly plastic clays will hold as much as 75 per cent of their weight of water as compared with only 20 per cent in some coarse sands. Rohland suggests that the saturation point is reached when sufficient water is taken up to convert the colloids into the sol form. A thoroughly dried clay is very hygroscopic, adsorbing moisture from the atmosphere sometimes up to 15 per cent of its weight without becoming appreciably moist.⁵

In the manufacture of ceramic ware, it has been found that each kind of clay requires a fairly definite amount of water for satisfactory manipulation. Since no certain method has been devised for ascertaining when the correct proportion of water has

¹ E.g., Asch and Asch: "The Silicates in Chemistry and Commerce," London.

² JOHNSON and BLAKE: *Am. J. Sci.*, [2] **43**, 351 (1867); BIEDERMANN and HERZFIELD: Ries' "Clays," 123 (1914); COOK: *N. J. Geol. Survey, Rept. on Clays*, 287 (1878); VOGL: *Compt. rend.*, **110**, 1199 (1890); BOURRY: "Treatise on Ceramic Industries," London (1911).

³ GILE, MIDDLETON, ROBINSON, FRY, and ANDERSON: *U. S. Dept. Agr. Bull.* 1193 (1924).

⁴ Colloid Symposium Monograph, **2**, 132 (1924); KING: *Wis. Agr. Exp. Sta.*, 6th Rept., 189, (1889); ALWAY and McDOLE: *J. Agr. Research*, **9**, 27 (1917).

⁵ BRIGGS and SHANTZ: *U. S. Dept. Agr. Bur. Plant Ind. Bull.* 230 (1912).

been added, this must be left to the workman. The usual method consists in adding enough water to make a paste that readily receives the impression of the fingers but does not stick to the skin. When water is added slowly to a moderately plastic dry clay in increasing quantities, the clay can be molded with difficulty at first, then more easily, and finally with the greatest facility. After this point is reached, more water causes it to become sticky and finally fluid. A highly plastic clay subjected to the same treatment becomes sticky and cannot be worked unless some non-plastic material is added.

Clay, like the hydrous oxide gels, shrinks on drying, the amount depending on the water content which, in turn, depends on the amount and nature of the colloidal matter. In order that ceramic ware may not warp or twist during the drying, it is essential to keep down the shrinkage as low as practicable. This is accomplished by the addition of suitable non-plastic material in amounts short of that which will seriously reduce the strength of the product. Ries¹ gives figures on a Herbertsville, N. J. clay which show that the addition of 40 per cent of sharp sand reduces the amount of water required for molding, more than 50 per cent. At the same time, the air shrinkage is reduced 38 per cent but this is accompanied by a loss of 40 per cent in tensile strength.

The adsorbing power of the colloidal matter of clay for salts was recognized almost 80 years ago by Way² who pointed out also that the clay substance adsorbs the basic ion more strongly than the acid ion, a fact that has been confirmed repeatedly. The significance of this adsorption by soil colloids for conserving plant foods and for the production of soil acidity has been discussed elsewhere.³

Clays adsorb aniline blue, rosaniline, carmine, malachite green, fluorescene, aurin, and other animal, vegetable, and tar colors in amounts that have been assumed to be proportional to the amount of colloid matter in the clay. Indeed, the power of a clay to adsorb malachite green⁴ has been used for the quantitative estimation of colloid content. In view of the marked effect of

¹ "Clays," 157 (1914).

² *J. Roy. Agr. Soc.*, 11, 313 (1850).

³ WEISER: "The Hydrous Oxides," 403-414 (1926).

⁴ ASHLEY: *U. S. Geol. Survey Bull.* 388, p. 65 (1909).

the hydrogen ion concentration on the adsorption of gels such as those of the hydrous oxides,¹ it is obvious that the method cannot give comparable results unless the composition of the colloidal matter of the clays compared, is nearly the same and unless the dye adsorption is measured at the same hydrogen ion concentration. Gile and his coworkers² calculate the colloid content from a determination of the adsorption capacity of a sample of soil and of the colloidal material extracted from the soil. In this case, also, the adsorptions must be determined at the same hydrogen ion concentration if accurate results are to be obtained.

Deflocculation and Flocculation.—When a soft clay is shaken with water, the colloidal matter forms a sol consisting of negatively charged particles. The deflocculation is facilitated by the presence of electrolytes with strongly adsorbed anions such as an alkali hydroxide, carbonate, or silicate and is retarded or prevented by electrolytes with relatively strongly adsorbed cations.

It is well known that clayey matter carried to the sea by rivers is deposited quickly on reaching salt water, only a small fraction being carried to deep waters.³ Hall and Mouson⁴ determined the precipitation value of various chlorides, sulfates, and nitrates on a colloidal clay. The order of precipitating power of the cations beginning at the greatest is: hydrogen, aluminum > calcium, barium, magnesium > potassium > sodium; and the order of stabilizing power of the anion is: hydroxyl > sulfate > nitrate > chloride.⁵ The order of a series of acids beginning with hydrochloric, which has the highest precipitating power, is: hydrochloric > nitric > sulfuric > mono-, di-, and trichloracetic > acetic > oxalic, tartaric > amido acetic, citric, and phenol. The last three are without precipitating action. Bradfield⁶ found a clay to be precipitated at about the same hydrogen ion concentration for hydrochloric, sulfuric, phosphoric, and acetic acids but a greater acidity was necessary with citric acid.

¹ WEISER and PORTER: *J. Phys. Chem.*, **31**, 1383, 1704 (1927).

² U. S. Dept. Agr. Bull. 1193 (1924).

³ MURRAY and IRVINE: *Proc. Roy. Soc. Edinburgh*, **18**, 229 (1891).

⁴ *J. Agr. Sci.*, **2**, 251 (1907).

⁵ (*f.*, also, KERMACK and WILLIAMSON: *Proc. Roy. Soc. Edinburgh*, **45**, 59 (1925)).

⁶ *J. Am. Chem. Soc.*, **45**, 1243 (1923).

In line with Hall and Mouson's observations, Bradfield found that 1.4 milliequivalents of potassium are required to precipitate a certain clay sol when present as chloride, and 14 milliequivalents as hydroxide, while 10 milliequivalents of potassium are necessary with a mixture consisting of 19 parts of chloride and 1 part of hydroxide, and 14 milliequivalents with a mixture of 18 parts chloride and 2 parts hydroxide. The precipitation value of potassium chloride is but one-tenth that of potassium hydroxide since chloride ion is absorbed much less strongly than hydroxyl by colloidal clay. Mixtures of potassium chloride and hydroxide effect coagulation at some intermediate value. Obviously, the effect of hydroxyl ion will be much greater at relatively low concentrations on account of the proportionately greater adsorption; and above the saturation value for the adsorption of hydroxyl ion, which is reached sharply in the case of a strong adsorbent for a strongly adsorbed ion, the precipitation value of potassium ion is fairly constant. Another factor which may come in is that the presence of the strongly adsorbed hydroxyl ion, above the normal saturation value, may increase the adsorption of the precipitating cation to such an extent that the rate of precipitation in the presence of the mixture is greater than that of the same concentration of salt without any added hydroxide. This is apparently what happens in certain cases. Thus Mattson¹ finds the order of precipitating power of calcium compounds for a clay to be: chloride > sulfate, bicarbonate > hydroxide; but with slightly more than the precipitation value of calcium hydroxide, the rate of precipitation is faster than with salt concentrations considerably above the precipitation value. Similarly, low concentrations of sodium hydroxide stabilize a clay sol as evidenced by the higher concentration of calcium sulfate required for flocculation. But if the concentration of sodium hydroxide is as great as 0.002 *N* in a 1 per cent clay, the rate of precipitation is appreciably greater than with calcium sulfate alone, even when the concentration of the latter is considerably above its precipitation value in the absence of sodium hydroxide. Apparently, above a certain concentration, the influence of hydroxyl ion in increasing the adsorption of the precipitating calcium ion predominates over its own stabilizing

¹ *Kolloidchem. Beihefte*, **14**, 241 (1922).

action. The deflocculating power of calcium hydroxide is less marked than that of the alkali hydroxides because of the relatively strong precipitating action of calcium ion.¹ Comber² attributes the abnormal flocculating power of calcium hydroxide above a certain concentration to its coagulating action on emulgoid matter such as silicea that has a stabilizing action on the clay sol.³

In the preparation of pottery by the casting process, a heavy suspension of a suitable clay and non-plastic material, the clay slip, is poured into plaster of paris molds which absorb water from the suspension giving a solidified layer of the clayey material. The slip is left in the molds for a long enough time to give the desired thickness of wall, and the excess is then poured out. In view of what has been said concerning the relationship between water content of clay and shrinkage, it is important to keep the water content of the clay body as low as possible. This is accomplished by the addition of deflocculating electrolytes such as sodium hydroxide, sodium carbonate, and sodium silicate, the negative ions of which are adsorbed by the particles giving them a negative charge. In this way a slip may be prepared which is readily poured or cast, even though it contains less water than a stiff mass of clay and water without a deflocculating agent.

The pH value at which clay particles attain a maximum charge is lower for sodium silicate solutions than for sodium hydroxide or sodium carbonate. This is illustrated by Fig. 39⁴ in which the relative time of flow of a kaolin slip through an efflux viscosimeter is plotted against the sodium oxide content of the several deflocculating solutions. The greater deflocculating action of the silicate solutions is probably due to the presence of colloidal silica which adsorbs sodium ions, thus disturbing their equilibrium with the hydroxyl ions and allowing the latter to be adsorbed more readily by the clay particles than would be the case from a sodium hydroxide or carbonate solution. It is therefore necessary to specify the deflocculating agent employed.

¹ Cf. JOSEPH and OAKLEY: *Nature*, **117**, 624 (1926).

² *J. Agr. Sci.*, **10**, 426 (1920); **11**, 450 (1921); **12**, 372 (1922); *Nature*, **118**, 412 (1926).

³ Cf., also, HARDY: *J. Phys. Chem.*, **30**, 254 (1926); KERMACK and WILLIAMSON: *Nature*, **117**, 824 (1926); *Proc. Roy. Soc. Edinburg*, **47**, 202 (1927).

⁴ McDOWELL: *J. Am. Ceram. Soc.*, **10**, 225 (1927).

when giving the pH value at which a clay slip possesses its maximum fluidity. Silica sol alone does not serve as a deflocculating agent for clay.¹

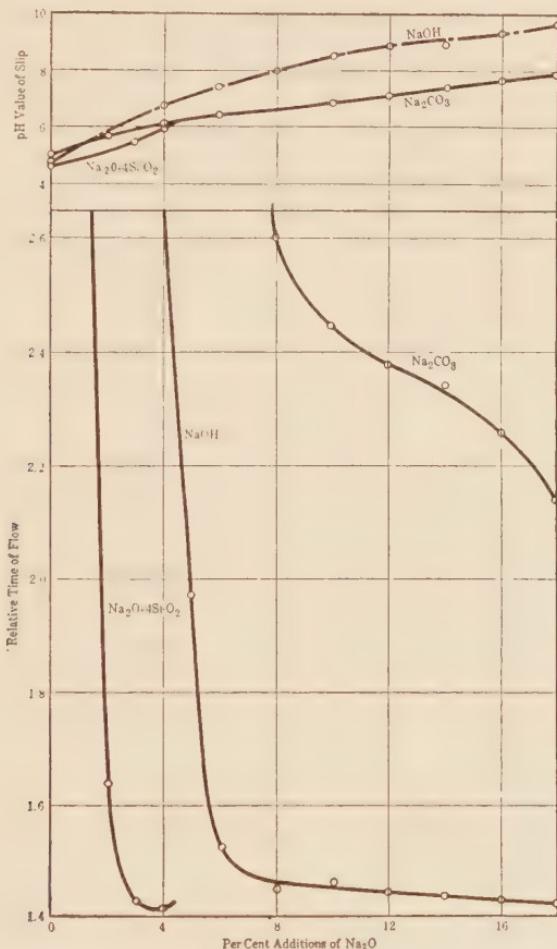


FIG. 39.—The action of deflocculating agents on a Florida kaolin.

The addition of a little acid to a clay slip causes it to flocculate to a stiff mass which will not fall from an inverted vessel. Bigot² has recently studied the effect of adding electrolytes to a number of semifluid clay suspensions prepared by grinding the several clays to an impalpable powder and mixing with water. The

¹ KERMACK and WILLIAMSON: *Proc. Roy. Soc. Edinburgh*, **47**, 202 (1927).

² *Compt. rend.*, **178**, 88 (1924).

electrolytes employed were the common mineral acids and alkalis, and the chlorides, carbonates, and silicates of ammonium, sodium, and potassium. In some cases a gel was obtained and in other cases a sol, the reason for which could not be explained. Unfortunately, the recorded data are too qualitative for anyone to interpret. Bigot merely added a "few drops" of the several electrolytes (unspecified concentration) to suspensions (unspecified concentration) of clays of unknown composition. So far as the mechanism of the deflocculation-flocculation process is concerned, his observations are valueless, therefore, except as an illustration of the kind of qualitative experimentation that is not helpful. It is well known that clays which contain appreciable amounts of soluble salts such as the sulfates of calcium and magnesium are difficult to deflocculate because of the precipitating action of the cation. On the other hand, clays containing protective colloids such as humus are easily deflocculated. In technical practice, tannin is sometimes added to facilitate the deflocculating action of the electrolytes and to increase the stability of the slip.¹

The addition of a small amount of alkali to a clay containing a considerable quantity of humus effects rapid deflocculation, but at higher concentration of alkali, a stiffening of the fluid material may result which is followed in a short time by a reliquefying of the mass. Neubert² has investigated these phenomena and quite correctly attributes the initial peptization to adsorption of hydroxyl ion which is greater in the presence of humus than in its absence. The stiffening at higher alkali concentrations is attributed in part to flocculation of the particles and in part to imbibition of water by the humus substances in the interior of the clay particles. This action on the deeper-lying layers liberates the humus which can again repeatize the clay particles and by interaction with humus, the alkali concentration is brought below the concentration range, where it exerts a sensible coagulation. The result is the reliquefying of the paste. At still higher concentrations, the mass does not undergo repeatization owing to exhaustion of the humus material.

¹ See p. 356.

² *Kolloidchem. Beihefte*, **4**, 261 (1913); cf. FODOR and SCHOENFELD: *Ibid.*, **19**, 1 (1924).

VI

MISCELLANEOUS COLLOIDAL SALTS

CHAPTER XXII

THE COLLOIDAL CARBONATES, PHOSPHATES, CHROMATES, AND ARSENATES

COLLOIDAL CARBONATES

Neuberg¹ prepared sols of the carbonates of calcium, strontium, barium, and magnesium by conducting carbon dioxide into a solution of the oxides of the respective metals in methyl alcohol. For example, from a solution of barium oxide in the alcohol, carbon dioxide threw down a thick gel which was subsequently peptized, giving a transparent sol of the consistency of thick collodion. On concentrating the sol by evaporation in vacuum, it set to a jelly which was repeptized by shaking with methyl alcohol. Evaporation to dryness gave a transparent celluloid-like mass.

Buzágh² modified Neuberg's procedure by passing dry carbon dioxide for several hours into a suspension of the ignited oxides in methyl alcohol and filtering off the residue. The clear sol could be diluted with alcohol, ether, benzene, and chloroform without coagulation. Acetone and carbon bisulfide gave flocculent precipitates and a little water caused the sol to set to a jelly from which crystals of the metallic carbonate separated in a short time. The dispersed phase of the sols was found to be not the normal alkaline earth carbonates but the dimethyl carbonates of the metals. The latter salts were obtained in a pure crystalline state by conducting carbon dioxide for several hours into methyl alcohol containing the finely divided oxides in suspension.

To prepare sols of the normal carbonates Buzágh passed carbon dioxide into a suspension of the metallic hydroxides in methyl alcohol and filtered off the residue. The alcohols were

¹ NEUBERG and NEIMANN: *Biochem. Z.*, **1**, 166 (1906); NEUBERG and REWALD: *Kolloid-Z.*, **2**, 321 (1908); NEUBERG: *Sitzungsber. akad. Wiss., Berlin*, 820 (1907).

² *Kolloid-Z.*, **38**, 222; **39**, 218 (1926).

converted to hydrosols by dialyzing against water. A more satisfactory method of preparing the hydrosols consists in decomposing the dimethyl carbonates of the metals with a small amount of water. These sols contain, besides the insoluble alkaline earth carbonate, some soluble bicarbonate and methyl alcohol which can be removed by dialysis. A study was made of the constitution and properties of a barium carbonate hydrosol prepared in this way. To prevent the sol from becoming basic, the dialysis was stopped before all of the bicarbonate was removed. In order to make the barium and carbonate content exactly equivalent, sufficient barium hydroxide was added to convert into carbonate the bicarbonate which was known to be present from an analysis of the supernatant liquid after coagulating a sample of the sol. Even when the amounts of barium and carbonate were equivalent, the intermicellar liquid was found to contain bicarbonate ion from hydrolysis of carbonate: $\text{CO}_3^{''} + \text{H}_2\text{O} \rightleftharpoons \text{HCO}_3' + \text{OH}'$. The constitution of the colloidal particles was deduced to be



with which are paired $2n$ HCO_3' ions. From the specific conductivity of a certain sol and its ultrafiltrate together with the mobilities of the colloidal particles and HCO_3' ions and the concentration of BaCO_3 , $\text{Ba}^{..}$, and HCO_3' , it was calculated that when $n = 2$, $x = 120$. The constitution of the particle was formulated $[120\text{BaCO}_3 \cdot \text{Ba}(\text{OH})_2 \cdot \text{Ba}^{..}]^{++}$, associated with two HCO_3' ions. The barium carbonate content of the particles was found to decrease with dilution and to increase with particle size, as one would expect.

While the above method may give the number of single molecules in a colloidal particle it would be well to have an independent confirmation by determining ultramicroscopically the number of particles in a given volume of a sol of known concentration. Since the barium carbonate sols contain particles of widely varying size, it is obvious that average values only will be obtained by either method.

While there is no objection to expressing the supposed composition of a colloidal particle by a formula, it should be recognized that colloidal particles, in general, are not complex ions of definite composition such as a cobalt amine cation or ferrocyanide anion.

The barium carbonate particle is a finely divided portion of solid that adsorbs the divalent barium ions more strongly than the univalent bicarbonate ions and so assumes a positive charge. The number of barium carbonate molecules in one of the solid particles will vary, of course, with the size and density of the particle which, in turn, are determined by the conditions of precipitation, the concentration, and the purity of the sol. While some may regard this view as too indefinite, it is quite as definite as is the composition of the colloidal particle which is determined by a number of variable factors that have not been evaluated quantitatively.

Barium carbonate sol is sensitive to the action of electrolytes. Since the particles show considerable variation in size, the sol can be precipitated fractionally by the step-wise addition of electrolytes, especially those with high precipitating power such as alkali hydroxide, sulfate, and iodate. It is claimed that

TABLE LII.—FRACTIONAL COAGULATION OF BARIUM CARBONATE
(Five cubic centimeters of sol mixed with 5 cubic centimeters of electrolyte)

NaOH, milliequivalents per liter	BaCO ₃ , not coagulated millimols	Li ₂ SO ₄ , milliequivalents per liter	BaCO ₃ , not coagulated millimols
0.0	125.6	0.0	126.6
0.25	123.8	1.0	121.8
0.50	121.2	2.0	98.8
1.00	91.8	2.5	73.2
1.25	67.2	3.0	48.1
1.50	39.1	3.5	27.5
2.00	7.7	4.5	5.2
K ₂ CrO ₄ , milliequivalents per liter	BaCO ₃ , not coagulated millimols	KIO ₃ , milliequivalents per liter	BaCO ₃ , not coagulated millimols
0.0	126.6	0.0	126.6
1.0	124.3	1.0	125.8
2.0	116.2	2.0	123.4
2.5	101.8	2.5	117.2
3.0	67.5	3.0	114.8
3.5	39.1	3.5	72.4
4.5	11.2	5.5	4.8

alkali halides and nitrates which precipitate only in relatively high concentrations do not cause fractional coagulation. It is much more likely, however, that the fractional coagulation with the latter salts is less marked and so was overlooked. Some observations on the fractional coagulation of the sol are given in Table LII and shown graphically in Fig. 40. It will be seen that the order of precipitating power of the anions is: OH > SO₄ >

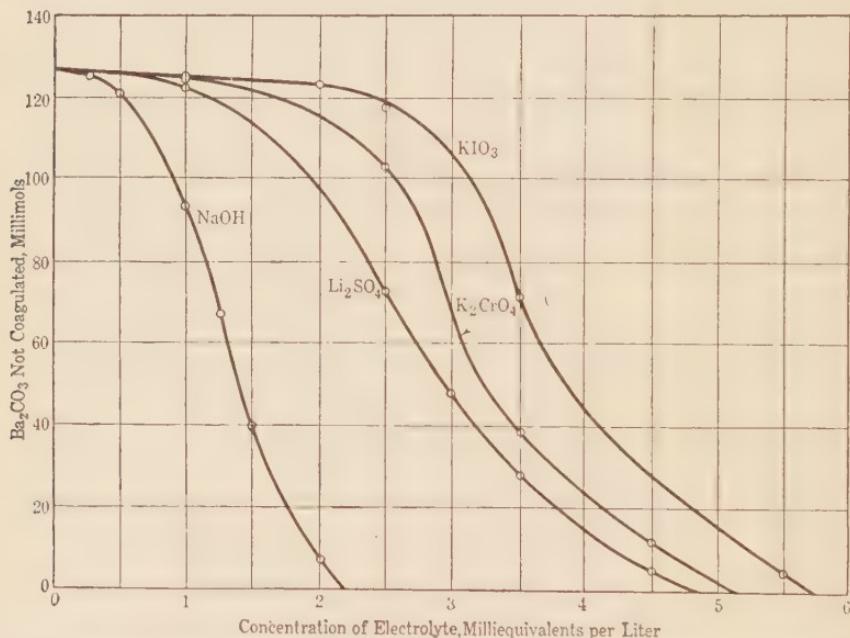


FIG. 40.—Fractional coagulation of barium carbonate sol by electrolytes.

CrO₄ > IO₃. As usual iodate which is taken to be a univalent ion behaves more like a divalent ion.¹

The close relationship between particle size and fractional coagulation is shown by the data given in Table LIII.

Colloidal carbonates are readily prepared by the use of protective colloids. Thus, colloidal carbonates of mercury,² lead,¹ and silver³ are formed in the presence of the so-called protalbinates

¹ Cf. WEISER and MIDDLETON: *J. Phys. Chem.*, **24**, 51 (1920).

² LEUZE: "Zur Kenntnis kolloidaler Metalle und ihrer Verbindungen" 21, 28.

³ PAAL and VOSS: *Ber.*, **37**, 3862 (1904).

and lysalbinates of sodium, and colloidal calcium carbonate by precipitation in the presence of albumin, gelatin, and peptone.¹

TABLE LIII.—RELATION BETWEEN FRACTIONAL COAGULATION OF BARIUM CARBONATE AND PARTICLE SIZE

K ₂ SO ₄ in 5 cubic centimeters added to 5 cubic centimeters of sol, milliequivalent	BaCO ₃ , not coagulated	Average diameter of particles in the uncoagulated sol, $\mu\mu$
0.0	147.2	198
0.4	143.0	178
0.8	128.0	148
1.2	73.0	89
1.6	28.0	77

COLLOIDAL PHOSPHATES

The slightly soluble orthophosphates of the alkaline earths and lead are precipitated in a gelatinous form by the interaction of alkali phosphate and the alkaline earth halides. Sols of these compounds have not been prepared in the absence of protective colloids. De Toni² made a sol of calcium orthophosphate by mixing hot solutions of sodium phosphate and calcium chloride in the presence of gelatin, gum arabic, blood serum, and starch. A sol is formed, also, by mixing dilute solutions of phosphoric acid and calcium hydroxide in the presence of gelatin. Hatschek³ obtained rhythmic bands of calcium phosphate by allowing calcium chloride to diffuse into a gelatin gel containing normal sodium phosphate. Phosphate clays possessing the properties of typical colloidal gels have been described by Elschner.⁴

Colloidal silver orthophosphate is formed by mixing 0.05 normal solutions of silver nitrate with a slight excess of 0.05 normal sodium phosphate or sodium hydrogen phosphate.⁵ The sol precipitates slowly on standing but it may be stabilized by adding sodium "lysalbinate" or "protalbinate."⁶

¹ SABBATANI and SALVIOLI: *Atti. r. ist. Veneto*, **71**, II, 1057 (1912); *Chem. Abstr.*, **10**, 1356 (1916).

² *Kolloid-Z.*, **28**, 145 (1921).

³ *Kolloid-Z.*, **27**, 225 (1920).

⁴ *Kolloid-Z.*, **31**, 94 (1922).

⁵ LOTTERMOSER: *J. prakt. Chem.*, [2] **72**, 39 (1905).

⁶ PAAL and VOSS: *Ber.*, **37**, 3862 (1904).

COLLOIDAL CHROMATES

Colloidal solutions of silver chromate are formed by bringing together silver nitrate and potassium chromate in the presence of gelatin or sugar.¹ It is probable that the chromates of lead, silver, and barium will form sols under similar conditions since they are less soluble than the silver salt. Lead chromate is peptized by a boiling concentrated solution of potassium nitrate.² When lead sulfate suspended in potassium nitrate solution is treated with potassium chromate, lead chromate is precipitated as a fluorescent greenish sol.³

The phenomenon of rhythmic precipitation was discovered in connection with silver chromate when Liesegang⁴ placed a drop of silver nitrate on a glass plate coated with moist gelatin containing a small amount of potassium dichromate and obtained the series of rings now so well known. A similar experiment can be carried out in a test tube, giving the so-called rhythmic bands. Numerous investigations with silver chromate and many other substances have been carried out with the end in view of determining the mechanism of the banding process. Ostwald⁵ attempts to explain the phenomenon by assuming that the silver chromate in Liesegang's original experiment remains in supersaturated solution, diffusing along with the silver nitrate until the metastable limit is reached when precipitation occurs. This ingenuous hypothesis has proven inadequate since the apparently clear spaces were found by microscopic examination to contain some very fine crystals which would prevent supersaturation.⁶ Bechhold⁷ believes that the precipitate which constitutes the bands is slightly soluble in the reaction product and hence that

¹ LOBRY DE BRUYN: *Rec. trav. chim.*, **19**, 236 (1900); *Ber.*, **35**, 3079 (1902).

² OECHISNER DE CONINCK: *Bull. acad. roy. méd. Belg.*, 665 (1909).

³ MILBAUER and KOHN: *Chem. Ztg.*, **48**, 1145 (1922).

⁴ *Phot. arch.*, **37**, 321 (1896); "Chemische Reaktionen in Gallerten," Dusseldorf (1898); *Z. anal. Chem.*, **50**, 82 (1911); *Kolloid-Z.*, **9**, 296 (1911); **12**, 74, 269 (1913); **16**, 76 (1915); *Z. physik. Chem.*, **88**, 1 (1914).

⁵ "Lehrbuch allgemeinen Chemie," 2nd ed., **2**, 778 (1911); cf. NOTBOOM: *Kolloid-Z.*, **32**, 247 (1923).

⁶ Cf. HATSCHEK: *J. Soc. Chem. Ind.*, **30**, 256 (1911); *Kolloid-Z.*, **8**, 193 (1911); **10**, 124 (1912); **14**, 115 (1914); *Proc. Roy. Soc. (London)* **99 A**, 496 (1921).

⁷ *Z. physik. Chem.*, **52**, 185 (1905).

new bands can form only after a point is reached where the concentration of the reaction products is sufficiently low. Wolfgang Ostwald¹ merely restates Bechhold's view when he says that probably all reactions giving Liesegang rings are balanced reactions, precipitation of a ring depending on certain critical concentrations of all the reactants. Bradford² suggests that one of the reacting solutes is adsorbed by the growing precipitate, thus giving zones which are practically free from it. Holmes³ attributes the phenomena to the conditions affecting the rate of diffusion. He points out that, according to Fick's law, the rate of diffusion is greatest when the difference in concentration of the ions in question in two contiguous layers is greatest, that is, just below the front of a precipitation band. As a result, the region near the band decreases in concentration of negative ion, for example, faster than does the space below. Finally, the positive ions have to advance some distance beyond the band to find such a concentration of negative ions that the solubility of the salt is exceeded and precipitation occurs with the formation of a new band. Fricke⁴ likewise takes the position that Fick's law of diffusion lies at the basis of all rhythmic banding. Fischer and McLaughlin⁵ are of the opinion that the diffusion may be interrupted temporarily by the formation of semipermeable membranes.

Just as the supersaturation theory is inadequate, so a theory which assumes a balanced reaction will not account for the fact that quite insoluble substances will form rhythmic bands under suitable conditions.⁶ Hatschek⁷ obtained rings of silver chromate in silica gel which were found to consist of two modifications of the salt; red or yellow needles, and larger crystals bluish violet in color. The remarkable fact was noted that many rings lie in the

¹ *Kolloid-Z.* (Zsigmondy Festschrift) **36**, 380 (1925).

² *Biochem. J.* **10**, 169 (1916); **11**, 14 (1917); **14**, 29, 474 (1920); **15**, 554 (1921); *Kolloid-Z.*, **30**, 364 (1922).

³ *J. Am. Chem. Soc.*, **40**, 1187 (1918).

⁴ *Z. physik. Chem.*, **107**, 41 (1923); cf., also, WILLIAMS and MACKENZIE: *J. Chem. Soc.*, **117**, 844 (1920).

⁵ *Kolloid-Z.*, **30**, 13 (1922); TRAUBE and TAKEHARA: *Kolloid-Z.*, **35**, 245 (1924).

⁶ Cf. BRADFORD: Alexander's "Colloid Chemistry," 795 (1926).

⁷ *Kolloid-Z.*, **38**, 151 (1926).

still yellow-colored gel and therefore the complete exhaustion of the reacting components in the gel under the last ring is not a necessary condition for the formation of another ring. This observation would seem to disprove the general validity of the theories of Bradford, of Holmes, and of Fischer and McLaughlin. Moreover, none of the theories take into account the specific effect of the jelly which appears to play an important role in certain cases as evidenced by the fact that rhythmic bands of certain salts are formed only in certain jellies. Thus, silver chromate forms bands in gelatin jellies but not in agar while lead chromate forms bands in agar but not in gelatin.

Instead of regarding Liesegang ring formation as essentially a phenomenon of supersaturation it seems advisable to follow up the suggestion of Sen and Dhar¹ who consider the rings to result from the periodic coagulation of a peptized sol. This avoids the two difficulties that crystals are present in the apparently empty spaces between the bands and that the nature of the jelly has an effect. While the details of the hypothesis still must be worked out, the suggestion furnishes a new point of attack on an old problem that has never been solved satisfactorily.

Lead chromate is a valued yellow pigment known as chrome yellow. The color varies from a light yellow to orange, depending on the conditions of precipitation and the subsequent treatment. The canary yellow product thrown down from a chromate solution with lead acetate or nitrate changes to an orange on washing. To maintain the desired yellow tone the precipitation is carried out in the presence of sulfate so that lead chromate and lead sulfate come down simultaneously. The role of the lead salt has been attributed by Habieh² to the formation of a double salt $PbCrO_4 \cdot PbSO_4$ or $PbCrO_4 \cdot 2PbSO_4$ but the existence of such compounds has not been established. Jableczynski³ attributes the stabilizing action of lead sulfate to lead ions which cut down the hydrolysis of lead chromate thereby preventing the formation of "chrome red," $Pb_2(OH)_2CrO_4$. This hypothesis

¹ *Kolloid-Z.*, **34**, 270 (1924); DHAR and CHATTERJI: *Ibid.*, **37**, 89 (1925); GANGULY: *J. Phys. Chem.*, **31**, 481 (1927).

² See AMSEL: *Z. angew. Chem.*, **9**, 613 (1896).

³ *Chem. Ind.*, **31**, 731 (1908).

appears untenable since lead sulfate exerts no stabilizing action unless it is precipitated simultaneously with the chromate. Moreover, lead sulfate is itself highly hydrolyzed¹ and it is not obvious how it could prevent the hydrolysis of the chromate. Göbel² suggests that the lead sulfate prevents the coalescence of the fine yellow particles of lead chromate into larger particles which are darker in color.³ This very plausible suggestion is treated lightly by Milbauer and Kohn⁴ who conclude from a microscopic examination of the crystals and the action of solvents on them, that the stable yellow pigment is a solid solution of lead sulfate and lead chromate. Since lead sulfate is more soluble than lead chromate, the former has a greater tendency to come down in crystals from dilute solution than the latter. For this reason, it is argued that the technical production of chrome yellow is carried out in very dilute solutions and with continuous stirring in order to induce the simultaneous precipitation of the substances as mixed crystals.

The observations of Milbauer and Kohn are not altogether convincing. The color of lead chromate is determined by the size of the particles and by the extent to which the basic salt "chrome red" is formed. Since the lead chromate-lead sulfate precipitate remains yellow, it means either that the particles which come down yellow do not grow on standing or the chromate does not hydrolyze. It is not obvious how the formation of a solid solution prevents these phenomena. On the other hand, if the chromate particles are surrounded by an adsorbed film of lead sulfate as suggested by Göbel, the stabilization is readily explained.

The products known as the "chrome reds" are bright red pigment formed by adding basic lead acetate to a solution of alkali chromate. Between these and the various "yellows" a large number of shades of chrome orange may be obtained.

¹ DOLEZALEK: *Z. Elektrochem.*, **5**, 335 (1889); **6**, 557 (1900).

² *Chem. Ztg.*, **23**, 544 (1899).

³ Cf. FREE: *J. Phys. Chem.*, **13**, 114 (1909); BOCK: *Farben-Ztg.*, **25**, 761 (1920); WAGNER and KEIDEL: *Ibid.*, **31**, 1567 (1926).

⁴ *Z. physik. Chem.*, **91**, 410 (1916); *Chem. Ztg.*, **46**, 1145 (1924).

COLLOIDAL ARSENATES

The addition of excess ferric chloride to a normal solution of disodium arsenate gives a sol which is said to be $\text{Fe}_2(\text{HAsO}_4)_3$ but which may be, at least in part, an adsorption complex of hydrous ferric oxide and arsenic oxide. This sol is precipitated as a jelly either by dialysis¹ until the concentration of the stabilizing hydrogen ion is reduced below a critical value or by the addition of a precipitating electrolyte.² The so-called aluminum arsenate sol prepared in the same way as the iron sol exhibits similar properties.²

As has been seen in the first chapter of this volume,³ von Weimarn's theory tells us that mixing dilute solutions which interact at once will not give a jelly since the percentage supersaturation $U = \frac{P}{L}$ ⁴ is too small because of the small value of P . As a matter of fact, however, jellies have been obtained under certain conditions by mixing quite dilute solutions in which P is small and in which L is sufficiently large that precipitation is slow and quantitative precipitation impossible so that $\frac{P}{L} = U$ is quite small. It is quite possible to obtain a gelatinous precipitate by mixing dilute solutions of two salts which precipitate immediately (P small, but L very small) but a jelly will not form under these conditions. The reason is evident when we consider the impossibility of getting the instantaneous mixing of the solutions, which is essential for uniform precipitation throughout the solution. One part is precipitated before another is mixed with the precipitant and the homogeneity which is characteristic of a jelly is lost. Moreover, the mixing itself will tend to destroy the jelly structure. The results are therefore not unlike those obtained when a colloid, capable of forming a jelly by slow precipitation, is coagulated too rapidly by the addition of excess electrolyte. To obtain a jelly from a colloidal solution it is

¹ GRIMAUX: *Compt. rend.*, **98**, 1540 (1884); HOLMES and RINFUSZ: *J. Am. Chem. Soc.*, **38**, 1970 (1916); HOLMES and ARNOLD: *Ibid.*, **40**, 1014 (1918); HOLMES and FALL: *J. Am. Chem. Soc.*, **41**, 763 (1919).

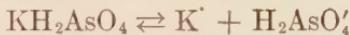
² WEISER and BLOXSON: *J. Phys. Chem.*, **28**, 26 (1924).

³ P. 7.

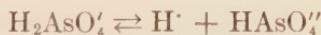
⁴ P is the amount of supersaturation at the moment precipitation begins and L is the solubility of the salt.

necessary to add such an amount of electrolyte that thorough mixing is possible before appreciable coagulation takes place. From these considerations it follows that precipitation of a hydrous substance as a result of double decomposition might form a jelly instead of a gelatinous precipitate in case the thorough mixing of the solutions could be effected before precipitation began and in case the precipitation, once started, proceeded at a suitable rate. Such conditions do not obtain as a rule; but they are quite possible theoretically. Thus the precipitation may be the result of a step-wise reaction, one step of which proceeds at a suitably slow rate. It is further possible to have a reaction that proceeds very slowly at low temperatures but with marked velocity at higher temperatures. This would not only allow of mixing without precipitation but would enable one to control the subsequent rate of reaction by a suitable regulation of the temperature.

Such a favorable combination of circumstances apparently obtains when a manganese salt of a strong acid and KH_2AsO_4 are mixed. The latter salt ionizes thus:



but on account of the solubility of $\text{Mn}(\text{H}_2\text{AsO}_4)_2$ no Mn ions are removed from solution by interaction with $\text{H}_2\text{AsO}_4'$. The latter ion, however, undergoes secondary ionization to a slight degree as follows:



and insoluble MnHAsO_4 is formed in accord with the following reaction:



Since the precipitation of MnHAsO_4 is accomplished by the formation of an equivalent amount of free hydrogen ion in solution, an equilibrium is set up which prevents the complete precipitation of the manganese. The amount of MnHAsO_4 formed, however, and the rate of formation by the above process are apparently influenced to a marked degree by the temperature, so that good jellies can be obtained by mixing dilute solutions of the necessary salts in the cold and allowing the mixture to stand at room temperature or warming to a suitable temperature. This has been demonstrated with the arsenates of manganese,

¹ DEISZ: *Kolloid-Z.*, **14**, 139 (1914).

cobalt, ferrous iron, cadmium, and zinc.¹ The results with manganese arsenate are recorded in Table LIV. Solutions of normal manganese chloride and KH_2AsO_4 were prepared from freshly boiled water. This precaution was necessary to prevent the formation of air bubbles in the jelly. The solutions were

TABLE LIV.—PRECIPITATION OF MANGANESE ARSENATE

Electrolytes mixed, cubic centimeters		Final volume	Nature of precipitate
MnCl ₂	KH ₂ AsO ₄		
10	10	20	Firm jelly, almost clear
10	20	30	Firm jelly, almost clear
10	20	50	Firm jelly, perfectly transparent
10	20	100	Firm jelly, perfectly transparent
10	20	200	Soft jelly, perfectly transparent
10	20	300	No jelly
NaH ₂ AsO ₄			
10	10	20	Cloudy jelly, not uniform
10	10	50	Cloudy gelatinous precipitate

cooled to 0° and suitable amounts of each were placed in 60-cubic-centimeter test tubes in the ratio shown in the table. The solutions were diluted with cold water to the final volume shown in column 3 or an aliquot part thereof. After rapid mixing the solution was set aside for 15 to 20 minutes and if jelling had not begun, the tube was warmed by dipping carefully into boiling water until precipitation started and was then allowed to stand quietly. The jellies obtained in this way are quite stable, showing little tendency to cloud up and crystallize on standing in the cold; but on heating, crystals of MnHAsO_4 are formed. Good jellies are not obtained with Na_2HAsO_4 since the precipitation is too rapid to allow time for mixing and the formation of the jelly structure.

The most important colloidal arsenates are the calcium and lead salts which are dusted or sprayed on plants or trees for the purpose of destroying insects. If the finely divided precipitated salts are suspended in water they assume a negative charge.

¹ WEISER and BLOXSON: *J. Phys. Chem.*, **28**, 32 (1924).

Since the surfaces of leaves possess a like charge, the insecticide does not adhere to them readily and is soon washed off by rain or dew. The particles of salt adhere much more tenaciously if they are prepared in such a way that they adsorb a positive ion which gives them a positive charge when wet. Thus, a positively charged basic calcium arsenate made under commercial manufacturing conditions, not specified, and tested in the field was found to possess an adherence from 196 to 259 per cent greater than the ordinary precipitated salt.¹

The lead arsenate precipitated from lead nitrate solution with disodium arsenate is the acid salt which does not become positively charged under ordinary conditions. On the other hand, the basic salt thrown down from lead acetate solutions readily assumes a positive charge.² The acid arsenate is assimilated to a greater degree than the basic arsenate; hence the former possesses higher insecticidal efficiency.³ The acid salt may be made adherent by coating the fine particles with a film of lead oleate.⁴ This is accomplished by suspending the salt in water containing a known amount of sodium oleate and adding an equivalent amount of lead acetate with vigorous stirring. The dried product is not wetted by water but the suspension spreads evenly on foliage and adheres firmly to the surface.

Woodman⁵ demonstrated that leaves can be wetted by a spray liquid provided the surface tension is reduced below a critical value said to be in the neighborhood of 32 dynes per centimeter.⁶ This can be accomplished cheaply by the addition of a small amount of soap. The maximum amount of spray liquid is retained at the critical surface tension. At higher tensions the wetting of the leaves is imperfect while at lower values the wetting power is not increased but the spreading power is greatly augmented. After the surface tension has been reduced to the point where the foliage is wetted perfectly, an increase in the viscosity

¹ MOORE: *Ind. Eng. Chem.*, **17**, 465 (1925); *J. Econ. Entomol.*, **18**, 282 (1925).

² MOORE: *Ind. Eng. Chem.*, **17**, 466 (1925).

³ LOVETT: *Oregon Agr. Expt. Sta. Bull.* **169**, 1 (1920); *Chem. Abstr.*, **15**, 3718 (1921).

⁴ VAN LEEUWEN: *J. Econ. Entomol.*, **18**, 744 (1925).

⁵ *J. Pomology Hort. Sci.*, **4**, 38 (1924).

⁶ Cf., however, ROBINSON: *J. Agr. Research*, **31**, 71 (1925).

of the spray liquid causes an increase in the amount of liquid retained as a film by the leaves. Hence, the use of gelatin in concentrations of about 0.3 per cent is advantageous. Moreover, gelatin¹ in concentrations between 0.5 and 0.2 per cent is a better stabilizer for lead arsenate sols than sodium caseinate, dextrin, starch, or soap.

¹ BRINLEY: *J. Agr. Research*, **26**, 373 (1923); WOODMAN: *J. Pomology Hort. Sci.*, **4**, 78, 95, 184 (1925).

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